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INVESTIGATION OF RADIOCATION SPECIATION AND ITS ENVIRONMENTAL CONSEQUENCES

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by

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SUMMARY

The object of the work performed and detailed in this report was to create a mathematical model able to predict the species and therefore, the mobility of radionuclides in receiving waters from uranium mining operations. In order to achieve this aim, environmental data at two locations (Quirke Lake in Ontario and Hidden Bay in Saskatchewan) were collected. These data served as input for average data files for the two localities and using speciation measurements of environmental samples, a speciation model adapted from the MINEQL system of Morel was constructed. This model was then calibrated using our environmental data and the final product is a mathematical model including thorium, uranium and radium that is able to predict the speciation of these elements in receiving waters. In addition, a separate model for interstitial water was also constructed.

Both models have been adapted so that they are able to operate on an IBM-PC with or without a 8087 Math Co-processor. This is the first time such a speciation model has been put on to an easily available computing system and it makes it available to a wide possible user cross section. The model can be adapted not only for pore waters and environmental site specific situations but can also be used to investigate the runoff of tailings and the interstitial water concentrations in tailings. By considering equilibrium with a particulate phase, the particulate distribution of metals can also be investigated. It is hoped that this model will be of wide interest and use to the uranium mining industry.

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1.0 INTRODUCTION

The work performed under this contract is part of the Measurements (fundamental studies) program initiated in 1982 by the National Uranium Tailings Program. The major objective of the present contract was to evaluate the importance of organic ligands on the environmental distribution of radiocations. The distribution of radiocations into their environmentally encountered physicochemical forms is influenced by many complex processes. The degree of association of such cations to a particular ligand in competition with other ligands is primarily a function of the alpha value of that association (i.e., the product of the cation and ligand concentrations and the stability constant of the associated moiety). The universal applicability of this relationship enables one to make some predictive judgements on the environmental fate of an element, provided the relevant data for ligand associations, concentrations and stability constants are known.

In this project, we have investigated the fate of radiocations in two ways. The first approach is of a practical nature. In this we have measured the physiochemical forms of pertinent elements and ligands. This information has helped us to better understand the effect of organic ligands in binding radiocations in the environment. The second approach was to produce a mathematical model of radiocation speciation, taking into account the effect of organic material.

In addition to these approaches, laboratory determinations of stability constant data of radium-226 with humic and fulvic compounds were also performed. This information was used to explain the field data and to expand the model.

These approaches have enabled us to demonstrate the importance of an element's speciation in the determination of its environmental fate and to produce a speciation model that includes selected radiocations and organic matter. The calibration of this model with the environmental data will enable the use of this model to help in predicting the fate of radiocations in the environment.

In addition, a contract amendment to adapt our program for use on an IBM/PC has enabled a much wider use of this model. It can be adapted for several environments and will be of considerable use to the uranium mining industry.

2.0 FIELD PROGRAM

The sampling program was designed to collect samples from two locations of different geology. The sites were chosen in consultation with the Scientific Authority, Roy John and Dr. Sharma of the University of Waterloo.

The first site was on Wollaston Lake in northern Saskatchewan (see Figure 2.1). The area chosen for investigation was Hidden Bay at the western end of the lake. This area is impacted with runoff from the Rabbit Lake Uranium Mine which has been operated by Eldorado Resources Ltd. for the past ten years. Effluent water undergoes pretreatment and flows through a marshy area to enter Hidden Bay in the north. Sample stations were selected so the input and potential impingement of this stream could be determined (see Figure 2.2). Due to the depth of the lake, samples other than that at the surface were only possible at stations 4 and 5. The sediment in this area has a considerable organic content, and the combination of this and the relatively high pH make the possible extent of organic material complexing radiocations considerably greater than in the Quirke Lake area.

It was decided that the second sampling area would be in the northwest portion of Quirke Lake in southern Ontario. This area has considerable background information and average concentrations of many chemical parameters can be obtained from the literature (see section 5). The sample area and the sites chosen for investigation are shown in Figures 2.3 and 2.4. The main influence on the sampling area, in terms of effluent input, is from the stream shown in the northwest of Figure 2.4. This stream contains effluent primarily from the Rio Algon Uranium Mine situated in the vicinity. However, Quirke Lake is surrounded by uranium mining operations and the general water quality of the lake will be also influenced by those operations that discharge effluent into the rest of the lake.

Hidden Bay samples were obtained between July 21 and 24 and Quirke Lake samples from July 26 to July 28. The sampling procedure at each location was the same.

After choosing a suitable site, the boat was anchored, then allowed to drift downstream to reduce the risks of contamination. The site was pinpointed on a map using a sextant and compass. The water depth at each site was measured and suitable sampling depths were chosen. Samples were collected using tygon tubing connected to a peristaltic pump. The sample tubing was looped at the input end and a stainless steel weight was tied below. This end was lowered to the correct depth and the pump was turned on. Temperature measurements at the sampling depths were taken using a submersible thermistor manufactured by Dobrocky Seatech Ltd. pH and E_h were measured first at each depth prior to the collection of water samples. All samples were filtered through 0.45 um cellulose acetate filters. At each station nutrient samples were collected first, followed by a 2 L sample for uranium analysis. The last sample collected was the 1 L trace metal sample. For each of these samples the container was washed with sample, filled once, filled again and capped. The filters used for the 2 L samples then were stored for the determination of particulate organic carbon (P.O.C.). After all the water samples had been collected, a bottom grab was obtained. Sediment samples (10 g x 2) from the middle of the grab were collected for pore water analysis.

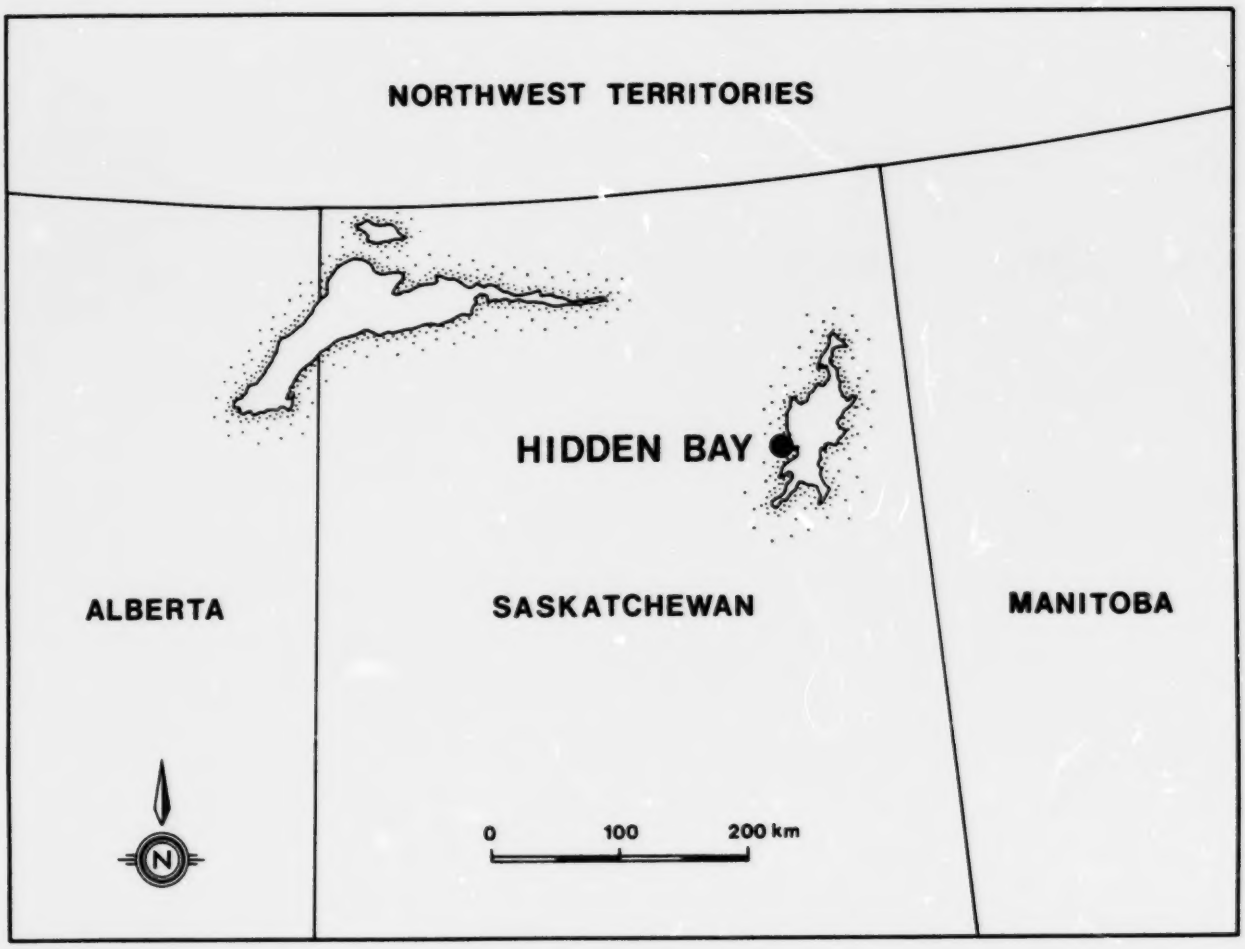

Figure 2.1 Location of Sampling Area in Northern Saskatchewan.

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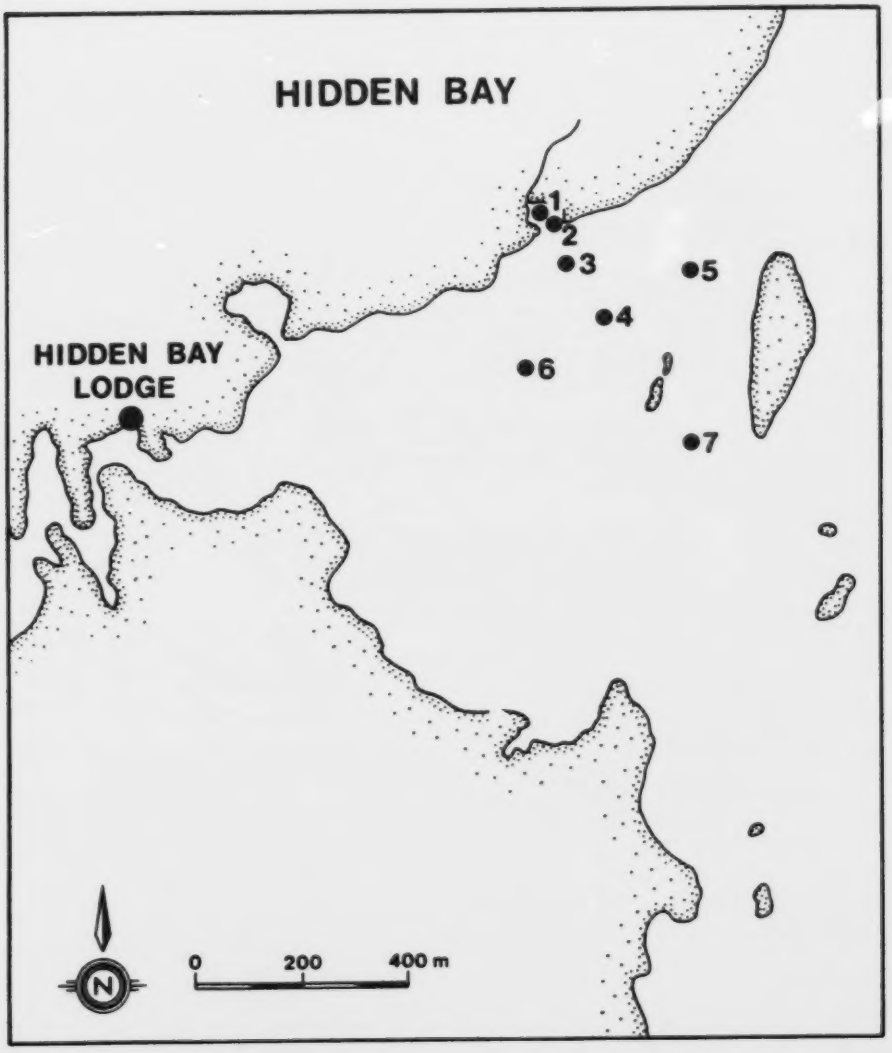

Figure 2.2 Location of Sampling Stations In Hidden Bay.

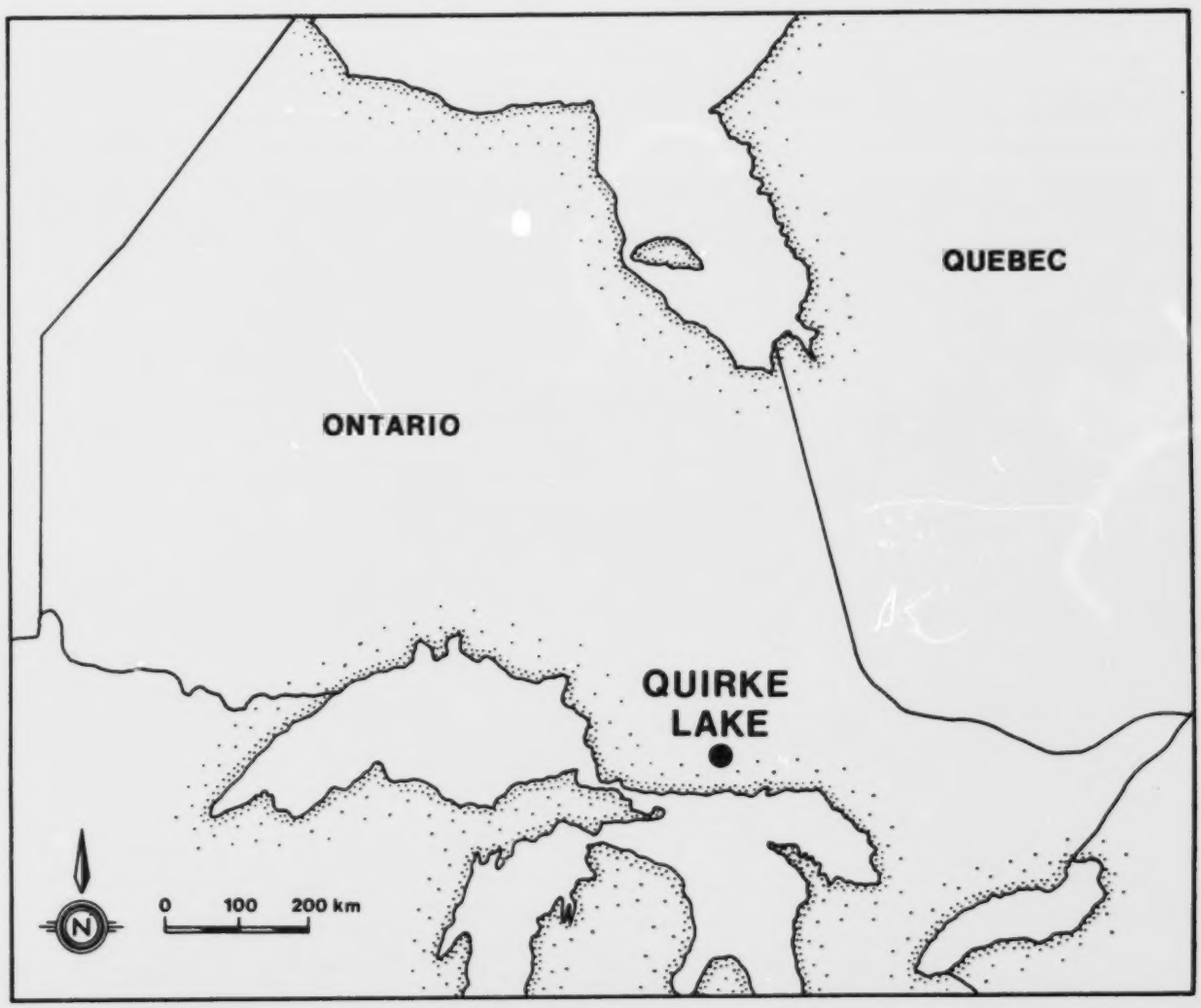

Figure 2.3 Location of Sampling Area in Southern Ontario.

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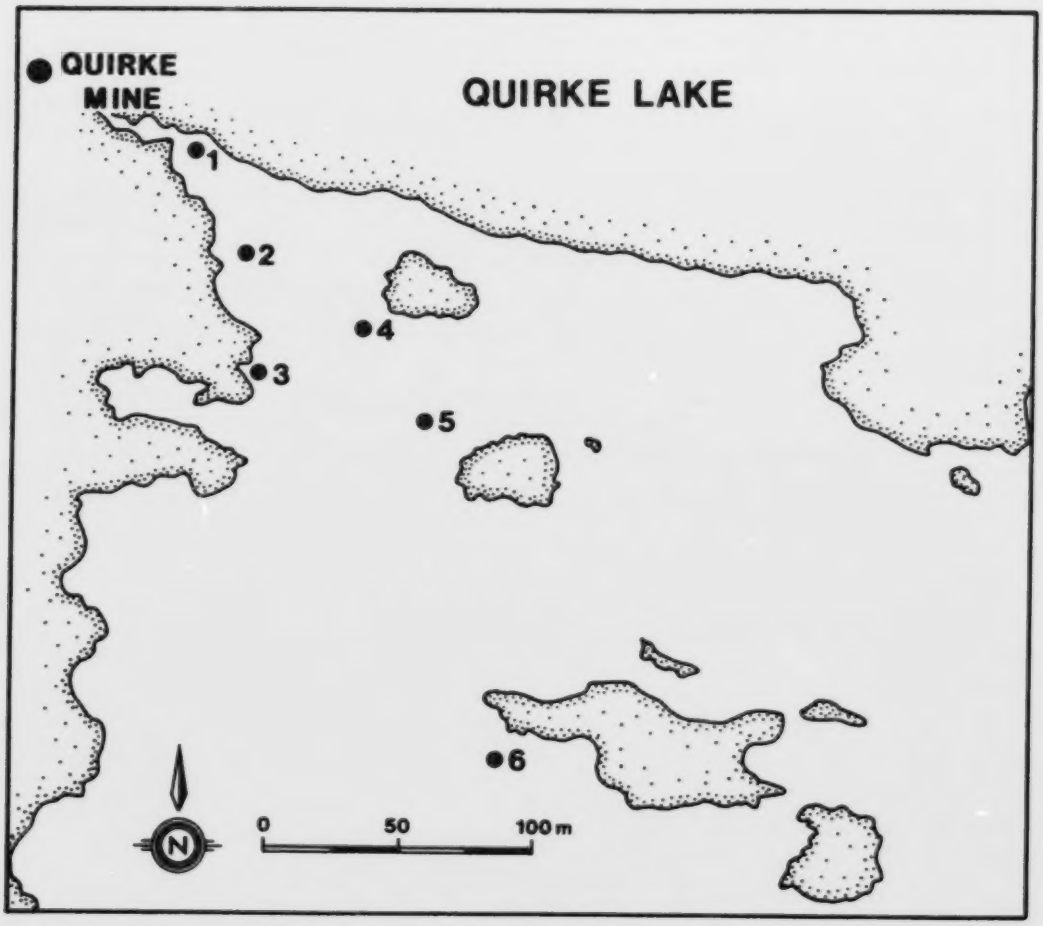

Figure 2.4 Location of Sampling Stations in Quirke Lake.

3.0 ANALYTICAL METHODS

Samples taken from Quirke Lake and Hidden Bay were analyzed for several components. An outline of these determinations is shown schematically in Figure 3.1. The details of methods used for each of these analyses are given in this section.

3.1 ALKALINITY

This method was based on the Environment Canada, 1981 (Naquadat No. 10101) method for calculating total alkalinity. The 1 mL sample was diluted in distilled water and a potentiometric titration was carried out using a standard solution of acid. A two-end-point technique was employed that determined the actual inflection point pH of the titration.

Reagents

Hydrochloric acid stock solution (0.10M) was prepared by diluting 0.9 mL of concentrated HCl (Baker Instra-analyzed) to 100 mL. This solution was further diluted by 1:10 to give 100 mL of 0.01M HCl titrant solution.

Standardization Solution was prepared by dissolving dry anhydrous Na_2CO_3 (1.0003 g Fischer Cert. ACS) in 100 mL of distilled water.

Standard commercial buffer solutions of pH 4.01 and 6.86 were also prepared.

Standardization

A Metrohm Dosimat burette (5.00 mL) was filled with hydrochloric acid titrant (0.01M) and the 'F' factor standardization was performed by titrating 100 uL of the standardization solution as follows. A combination pH electrode was calibrated using buffer solutions at pH 4.01 and pH 6.86

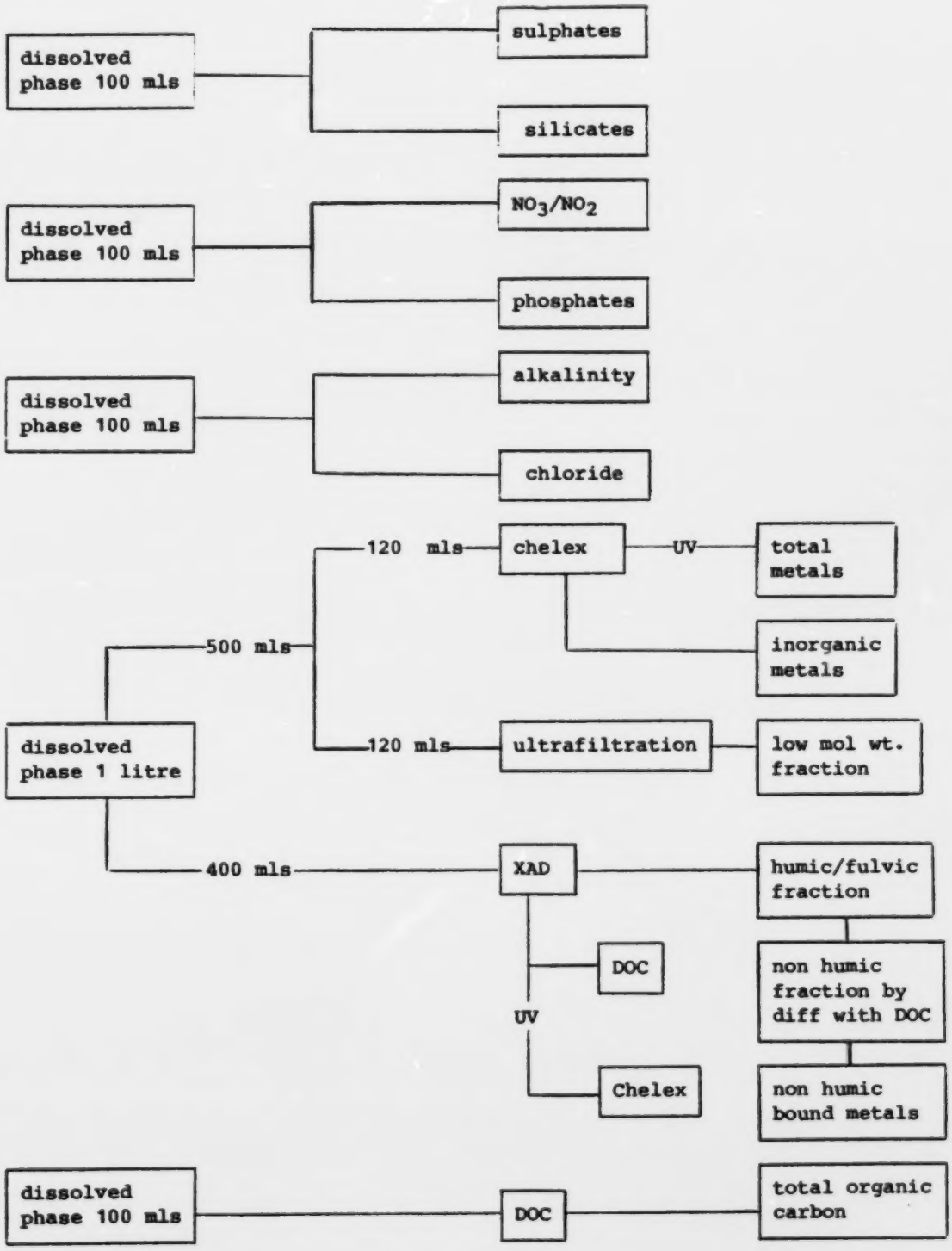

Figure 3.1 Schematic of Analyses

and 100 uL of Na_2CO_3 standardizing solution was pipetted into a dry 4-dram vial. Exactly 5 mL of distilled water was added while stirring. The electrode was lowered into the solution so that the tip was completely immersed, but above the stir bar. The solution was titrated to pH 4.5 and 4.2 and the volume of acid at both pH values was recorded. Standardization was carried out in triplicate. The 'F' factor was determined for analyses of Hidden Bay samples and again for the Quirke Lake samples.

Samples Analysis

Water samples were analyzed in duplicate. The sample (1 mL) was placed into a clean dry vial and 5.0 mL of distilled water was added. The Finnpipette was rinsed with each different sample to prevent cross contamination. Solutions were magnetically stirred and solution titrated with acid to pH 4.5 and pH 4.2, as with 'F' factor standardization. Both burette tip and pH electrode were wiped and rinsed between samples.

The alkalinity samples collected from Hidden Bay and Quirke Lake were kept frozen until just prior to analyses. The Hidden Bay samples were analyzed immediately after thawing at room temperature. There was insufficient time to analyze the thawed Quirke Lake samples. These were refrozen and thawed again the next day. The samples remained at room temperature for a few days before analyses were carried out. Remaining samples were refrozen to be used later in chloride analysis.

Calculations

The alkalinity of the samples was calculated using the following formula.

$$\text{Total Alkalinity} = F\,[X_1 - (X_2 - X_1)] = F(2X_1 - X_2)$$

where alkalinity is expressed in mg/L $CaCO_3$

Where:

X_1 = mL of acid needed to titrate to pH 4.5

X_2 = mL of acid needed to titrate to pH 4.2

F = Standardization Factor

3.2 CHLORIDE

This titrimetric method, modified after that described in APHA (1975), applies to chloride determination in both filtered and unfiltered water samples.

Chloride ion is titrated with mercuric nitrate to form soluble, slightly dissociated, mercuric chloride. At the endpoint, the indicator diphenylcarbazone forms a purple complex with excess Hg^{+2} ions. The range of the method is 0.3 - 50.0 mg/L Cl^-.

Reagents

Standard Sodium Chloride (0.0141 N) was prepared by dissolving 824.14 mg of dried (140°C) NaCl in Milli-Q water and diluted to 100 mL.

Indicator-acidifer Reagent was prepared by completely dissolving 0.251 g s-diphenylcarbazone in 100 mL of 95% ethanol (OmniSolv). In the fumehood, 4.0 mL concentrated HNO_3 (Baker Instra-Analyzed) was then added dropwise to the solution which was magnetically stirred while adding 0.030 g xylene cyanol FF. This solution was stored in a dark glass bottle kept in a refrigerator.

Standard Mercuric Nitrate titrant (0.0141 N) was prepared by dissolving 2.5 g $Hg(NO_3)_2$ in 100 mL Milli-Q water containing 0.25 mL concentrated HNO_3 (Baker Instra-Analyzed) and making up to 1 L with Milli-Q water.

Standardization

Standard NaCl solution (50 mL) was pipetted into a beaker and diluted to 100 mL with Milli-Q water. The indicator-acidifier reagent (1.0 mL) 0.020 g $NaHCO_3$ was then added and solution was titrated, while stirring, with $Hg(NO_3)_2$ solution to a purple endpoint.

Sample Analysis

Sample (50 mL), Milli-Q water (50 mL), indicator-acidifer reagent (1 mL) and $NaHCO_3$ (20 mg) were combined in a beaker and titrated with standard $Hg(NO_3)_2$ solution, to a purple endpoint. A blank titration was performed on 100 mL Milli-Q water. The pH of all samples was measured after each titration and in all cases, the pH was in the range 2.4 to 2.6.

The samples for chloride analysis were the same as those used for alkalinity determinations. The samples had been refrozen after the alkalinity measurement. Hidden Bay samples and Quirke Lake samples were analyzed for chloride on different days. Samples were thawed prior to analysis.

Calculations

1. Normality of $Hg(NO_3)_2$

$$N = \frac{0.0141 \times 50.0}{V_1}$$

2. Chloride Concentration

$$[Cl^-] = \frac{35{,}500\ N\ (V_2 - V_3)}{V_4}$$

where:

N = normality of $Hg(NO_3)_2$

V_1 = Vol $Hg(NO_3)_2$ for standardization (mL)

V_2 = Vol $Hg(NO_3)_2$ for sample (mL)

V_3 = Vol $Hg(NO_3)_2$ for blank (mL)

V_4 = Vol of sample (mL)

$[Cl^-]$ = concentration of Cl^- in mg/L

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3.3 NUTRIENTS

Nutrient analyses were carried out by standard automated techniques utilizing Technicon autoanalyzer equipment. Dissolved nitrates (plus nitrites), silicates and orthophosphates were analyzed simultaneously using a Technicon sampler II, proportioning pump III, appropriate analytical manifolds and three Technicon single channel colorimeters.

A Pharmacia dual channel recorder and a Varian Vista 401 data processor were used to provide analytical plots.

The stock standard solution for each nutrient was calibrated using Sagami standards of known nutrient content. Calibration standards were prepared fresh daily and run after every 20 samples in order to correct for instrument drift. All standard values obtained after one day's analysis were used in a linear regression program from which sample values were interpolated.

Silicate

Reactive silicate was determined using an automated procedure based on Technicon Industrial Method No. 186-72W (Revised June, 1977). The silicates react with ammonium molybdate in an acidic medium to form β -molybdosilicic acid which was subsequently reduced, using ascorbic acid, to form 'molybdenum blue'. The intense blue colour of this compound was measured using a colorimeter at 660 nm (Grasshoff, 1969). Oxalic acid was added to the sample stream before the addition of ascorbic acid to eliminate interference from phosphates.

The range of the method is 0.2 to 75 ug-at Si/L.

Nitrate plus Nitrite

The automated procedure used for nitrate plus nitrite determination was derived from Technicon Industrial Method No. 158-71W (revised June, 1977). The sample was passed through a coil containing a copper-cadmium reducing agent (Armstrong et al., 1967; Grasshoff, 1969) to reduce nitrate to nitrite. The resulting nitrite, plus that originally present, was then reacted with sulphanilamide under acidic conditions to form a diazo compound. A coupling reaction was carried out on the diazotized sample by the addition of N-(1-naphthyl) ethylenediamine dihydrochloride to form the azo dye. The intensity of this dye was measured using a colorimeter at 550 nm.

The range of the method is 0.1 to 100 ug-at N/L.

Orthophosphate

The automated procedure used for phosphate analysis was developed by Technicon but includes modifications by Byrnjolfson (1973). The procedure involved formation of molybdophosphoric acid through reaction of the phosphate present with ammonium molybdate and potassium antimonyl tartrate. This was reduced by ascorbic acid to form a complex with a 'molybdenum blue' colour. The presence of antimony increased the reaction rate and intensified the blue colour. The concentration of the coloured complex was determined colorimetrically at 880 nm (Murphy and Riley, 1962).

The range of the method was 0.01 to 7.0 ug-at P/L.

3.4 SULPHATE

Sulphate analyses were carried out as described in Environment Canada (1981). The method is applicable to surface and groundwaters in the 1-40 mg/L sulphate range. Technicon autoanalyser equipment, outlined in the nutrient method (Section 3.3), was ultilized for this technique along with a Pharmacia dual channel recorder and a sulphate analytical manifold.

Sulphate ion in the sample was reacted with an equimolar solution of barium chloride and methylthymol blue at pH 2.5-3.0. Sulphate present in a water sample forms barium sulphate. After permitting sufficient time for this formation, the pH was adjusted to 12.5-13.0. Barium ions remaining in solution complexed with methylthymol blue to produce a blue colour, leaving an amount of grey uncomplexed methylthymol blue. The sulphate concentration was calculated by measuring the absorbance of the uncomplexed methylthymol blue solution at 460 nm using a colorimeter.

3.5 DISSOLVED ORGANIC CARBON METHOD

Dissolved organic carbon was determined by the ampoule technique following the standard procedure as given in Airey and Hogan (1980). All glassware used was first baked at 500°C for a minimum of four hours. Water for blanks and standards was freshly quartz distilled into glass containers. Three aliquots of each sample were pipetted into glass ampoules and then treated with approximately 0.12 g potassium persulfate and 0.2 mL 6% H_3PO_4. Six to ten replicate standards, ranging in concentration from 0.25 to 10.0 mg C/L, and blanks were prepared simultaneously. Sample size throughout was 3.0 mL. Flame sealing was performed on an Oceanography International Carbon (OIC) flame sealing unit, using a purge time of five minutes. The sealed ampoules were then autoclaved at 15 psi; 124°C for one hour. Carbon analyses was carried out on an IOC analysing unit following the procedure recommended in the manual.

3.6 CONCENTRATION OF METALS BY CHELATING RESIN

The metal content of the water samples was determined using an adaptation of the procedure of Kingston et al. (1978). In this procedure, transition metals are concentrated on Chelex resin (Riley and Taylor, 1968) and then eluted with acid. In our procedure, a pre-elution wash with ammonium acetate is used to remove alkaline earth metals that interfere with the atomic absorption detection step.

Water samples were passed through columns containing Chelex 100 resin (200-400 mesh) in the Ca^{2+} form to bind trace metal ions. The columns were then washed with ammonium acetate to remove alkaline earth metal ions, and finally eluted with nitric acid to collect the trace metal ions. Elements were then determined by graphite furnace atomic absorption spectrophotometry (GFAAS).

All equipment used was first soaked in 30% HNO_3 for a minimum of four hours, then in 0.1% HNO_3 for a minimum of one day, and finally rinsed in quartz distilled (QD) water. Reagents used were ultra-pure Seastar reagents (sub-boiling distilled). All procedures, except final analysis on the GFAAS, were carried out in a class 100 clean air laboratory.

A slurry of Chelex 100 was prepared by adding 120 mL QD water to 150 mL of new resin. The resin was allowed to settle and the water decanted. Further cleaning using this procedure involved addition of two more aliquots of QD water, five aliquots of 2 M HNO_3, three rinses with QD water and finally three to four aliquots of redistilled NH_4OH. The resin was then stored in NH_4OH solution until required.

Two columns were prepared for each sample. A bed volume (BV) of 4.5-5.0 mL Chelex 100 resin was poured into each column, caps were fitted and then one column was placed on top of the other to form a double column. Pump tubing, passing through a Technicon proportioning pump, was connected to the caps. For small sample volumes, for example <150 mL, the tubing was set up to deliver 1 mL/minute. For larger volumes a setting of 4 mL/minute

was used. The columns were first rinsed of excess NH_4^+ ions with 2.5 BV of QD water. This was followed by three bed volumes of $CaCl_2$ and 2.5 BV of QD water. The preweighed samples were then pumped through, followed by 12 BV ammonium acetate of pH 5.0 to pH 5.2, and 2.5 BV QD water. Dry, preweighed collection bottles (either 30 mL polyethylene bottles or 15 mL Teflon vials) were placed under the columns, and 2.5 - 3 BV of 2 M HNO_3 was eluted into these. The columns were eluted with a second aliquot of 2.5 - 3 BV 2 M HNO_3 into a fresh bottle. The bottles were reweighed to obtain an accurate volume. Blanks were run alongside the samples.

The results from the GFAAS analyses were first corrected for instrument drift, then blank corrected using the average of the results for the blanks run concurrently with the samples. Any samples within $\pm$ 3 s of the blank were considered to be less than the detection limit.

3.7 ORGANICALLY BOUND METALS

Selected metals were investigated for their association with organic ligands. This was performed in several ways and the methods employed are outlined below.

3.7.1 XAD Resin Separations

The method of Mantoura and Riley (1975 and 1978) was used to separate metals complexed by organic substances from natural waters. A column of XAD-2 resin is used to selectively adsorb the organic matter (and consequently metals bound to it). Amberlite XAD-2 resin is a macro reticular, non-polar, styrene-divinyl benzene copolymer. It is produced in the form of white, insoluble beads designed for either batch or continuous (column) operations. XAD-2 adsorbs both neutral and acidic organic compounds from water. A major environmental use of this resin has been the study of naturally-occurring, dissolved organic materials, including humic substances, present in both marine and fresh waters. The adsorption

of organic acids, such as humic substances, is determined by the aqueous solubility of the solute and the pH of the solution. At low pH (pH 2 is widely used), weak acids are protonated and adsorbed on the resin; at high pH, weak acids are ionized and desorption occurs. Water samples are generally acidified with HCl, passed through the resin column, and the absorbed organic acids are recovered by eluting the column with a basic solution, usually 0.1 M NaOH. Methanol-NH_4OH mixtures have also been used for elution of humic substances. Some work has been carried out to determine the adsorptive mechanisms involved in the concentration of organic solutes from water using XAD-2; van der Waal's forces, dipole interactions and hydrogen bonding are thought to be important. The organics collected in this way were eluted from the column and trace metals determined in the eluate.

Sample Preparation

The samples used for XAD resin separation were aliquots of those used for Chelex concentration. The samples were frozen after the Chelex analyses and thawed prior to XAD separation. Twelve samples were passed through the XAD resin. They were as follows:

HB-1-0.5	HB-2-1	QL-1-0.3	QL-3-1
HB-3-1	HB-4-1	QL-3-4	QL-4-8
HB-5-1	HB-6-1	QL-5-1	QL-5-8

About 400 mL of each sample was used. The sample bottle, cap, and sample were weighed. The empty bottle and cap, after all the sample passed through the column, was weighed. The difference in weight was the volume of sample that passed through the column. Blank samples of QD water, the same volume as the samples, were also passed through columns. Each sample was acidified to pH 2.2 with concentrated, ultra pure HCl (Seastar).

Reagents

Sodium Hydroxide (0.5 M) was used to condition the column. This was prepared by dissolving 20 g of NaOH pellets in quartz-distilled (QD) water (2 L). The solution was stored in a plastic, acid washed bottle.

Ammonium Hydroxide 2 M (for elution mixture) was prepared by diluting 105 mL of ultra pure, concentrated ammonia (Seastar) with 750 mL of QD water; the solution was stored in a plastic, acid washed bottle.

Eluting Solution was prepared by mixing equal volumes (250 mL) of methanol (Omnisolv) and 2 M ammonium hydroxide.

Procedure

The XAD-2 resin (160 g) was washed thoroughly by vigorously shaking a mixture of resin and 300 mL of QD water. The mixture was allowed to settle, and the water decanted (some fine resinous material was also lost). Washing was repeated three times. This procedure removes excess chloride. Washed resin was then extracted with acetone using a soxhlet apparatus to remove antibacterial agents and preservatives.

The extraction was carried out for two hours after which the resin was washed several times with QD water.

Column separations were carried out in the class 100 clean room. The procedure and set up for the separations was the same as for Chelex separations. Resin was poured as a slurry, into plastic acid washed columns, tapping gently to remove air bubbles; for each sample, two columns were poured and then one stacked upon the other; the top column retains the organic matter, the bottom column is the column blank. Each column pair was washed with 2-3 bed volumes of QD water, followed by 10 bed volumes of 0.5 M NaOH (the conditioning solution). Column pairs were rinsed with 2-3 bed volumes of QD water, then each sample was passed through a different column pair, at a flow rate of 4 mL/min.

The column pairs were separated and eluted with 5 bed volumes of the elution mixture. The eluate was collected from each column in a dry, preweighed, acid washed plastic bottle (weigh bottle cap as well). Eluates were stored in bottles with caps on, and the weight of each bottle (with cap) was recorded.

Methanol and ammonia were removed from the eluate by evaporation, and the metal-organic complexes broken up by ultra-violet irradiation before determination of trace metals. The bottles were left open for two weeks in the clean room to evaporate methanol and ammonia. The volume was reduced by about 50%. The total weight of bottle, cap and sample was recorded after evaporation. The samples were then acidified with concentrated HNO_3 (Seastar), by adding 100 uL of acid to each sample. The samples were then irradiated in quartz tubes, with ultra-violet light, for three hours. The sample, bottle and cap was then weighed again before analysis for trace metals.

3.7.2 Ultrafiltration

An alternative method for examining complexed metal is that of ultrafiltration. With this procedure, samples are filtered through a membrane of sufficiently small size to differentiate between organically bound and "free" metal ions. Ultrafiltration is a means of separating macromolecules according to molecular size, by filtration through a membrane under an applied gas pressure. The method is similar to reverse osmosis and differs only in the size of particles which pass the membrane. The membranes are usually thin sheets of polyelectrolyte complexes of polyanions and polycations, supported on porous polyethylene bases. Although they are designated by nominal molecular weight cut offs, these are dependent on various parameters of the compound being filtered, such as its size, shape and charge. Ultrafiltration membranes neither completely retain substances with molecular weights above a precise cut off, nor entirely allow substances with molecular weights below it to pass through. As a general rule, a given membrane will retain 75-80% of a compound with a molecular weight greater than the stated cut off.

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Interactions between the solute molecules themselves and between solute molecules and the ultrafiltration membranes can affect the ultrafiltration process. Aggregation effects, caused by complex formation involving reactive functional groups, can lead to increased retention of low molecular weight materials, such as fulvic acids. Geometrical factors are also important. The membranes are calibrated with globular materials and there are some indications that long chain polymeric substances of equivalent molecular weight, such as fulvic acids, are sterically hindered from passing through the membrane (Kwak et al., 1977). In the present work millipore CX10 ultra filtration membranes with a 1000 nominal molecular weight cut off were used.

In order to use these filters for trace metal and trace organic determinations careful cleaning of the filters is required. All tubing used is teflon and the filter holders are entirely made of quartz.

To clean the filters, each is placed in an acid washed quartz tube; 20 mL of QD water is sucked through the filter (the set up for this filtration apparatus is shown in Figure 3.2). This is then repeated with acid and alkaline solutions in the following sequence.

1.3 N HNO_3 - QD water - Isothermally distilled (ID) NH_4OH - (ID)NH_4OH - QD water - 1.3 N HNO_3

After this procedure the filter is rinsed with QD water that has previously been ultrafiltered as are the reservoir and teflon tube. Once this process is complete samples may be run.

Sample procedure

The quartz tubes are rinsed with a small quantity of sample as are the ultrafilters. The sample is then poured into the quartz tube and suction is applied to the end of the tube (see Figure 3.2). Just in front of the sample a small quantity of QD water can be observed separated from the

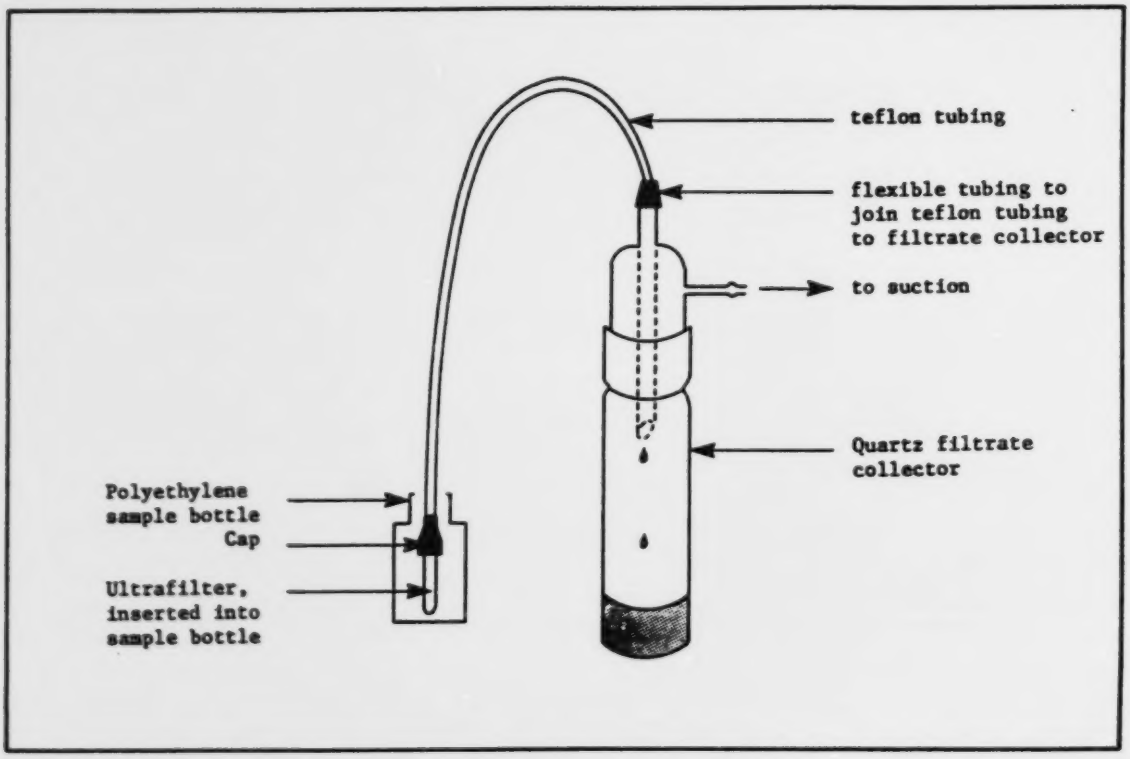
teflon tubing
flexible tubing to join teflon tubing to filtrate collector
to suction
Quartz filtrate collector
Polyethylene sample bottle Cap
Ultrafilter, inserted into sample bottle

Figure 3.2 Schematic Diagram of Ultrafiltration Apparatus.

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sample by a small air bubble. This is discarded and the collection vessel is then rinsed with 1-1.5 mL of ultrafiltered sample before the remainder is sucked through. One QD blank is run with every three samples and all these manipulations were performed in a Laminar flow hood inside a class 100 clean room. Once the ultrafiltration has been completed the metals may be concentrated by Chelex-100 resin.

3.8 SEDIMENT INTERSTITIAL WATERS

The frozen sediment samples were thawed in warm water and transferred to a glove box filled with high purity nitrogen at a positive pressure. The bags were opened, and the sediment was placed into a teflon squeezing unit containing a frit-supported 0.45 um millipore filter. The interstitial water was then squeezed from the sediment through the filter using nitrogen gas pressure.

The interstitial water was analyzed for nutrients and trace elements as previously described.

3.9 ATOMIC ABSORPTION ANALYSIS

The majority of the metals analyses for copper and iron were performed by graphite furnace atomic absorption spectrometry (GFAAS). Some of the lower level zinc analyses (largely from Hidden Bay) were also carried out by this technique.

The instrumentation used was a Varian AA-1475 atomic absorption spectrometer interfaced with a Varian GTA-96 graphite furnace, a Varian programmable sample dispenser and an Epson RX-80 printer. Operating conditions are summarized in Table 3.1. The programmable sample dispenser was programmed to set up a calibration working curve using a matrix blank and three standards prepared automatically by diluting a working standard with matrix blank. Sample injection size and the furnace operating program varied according to the element being analyzed.

Using a 'reslope' capability built into the GTA, the working curve was automatically re-established by running the matrix blank and the mid-concentration calibration standard after every eight samples.

In addition to this, calibration standards were placed among the samples (at intervals of 6-8 samples) in order to provide an instrument drift correction, if necessary, for the later processing of results. Samples and standards were run in duplicate with the mean value being used in later calculations.

All the zinc values for Quirke Lake samples, and a few Hidden Bay samples, were high enough for analysis by direct aspiration flame atomic absorption (FAAS) using the Varian AA-1475 and operating conditions as shown in Table 3.1. Some analyses for iron were also performed by FAAS.

A working curve was established using a matrix blank and three calibration standards to cover the range of sample values encountered. The working curve was checked after each sample reading by aspirating a standard of the nearest concentration.

Table 3.1 Operating Conditions (Varian AA-1475/GTA-95)

Element	Wave Length (nm)	Lamp Current (mA)	Slit Width (nm)	Method*	Detection Limit (ug/L)
Cu	324.8	4	0.5	GFAAS (20 uL injection)	0.2
Fe	248.3	5	0.2	FAAS: C_2H_2/Air	10
				GFAAS (20 uL injection)	0.1
Zn	213.9	5	1.0	FAAS: C_2H_2/Air	10
				GFAAS (20 uL injection)	0.01

NOTE: All analyses were performed using double-beam mode with deuterium continuum lamp background correction.

* FAAS: Flame atomic absorption spectroscopy
GFAAS: Graphite furnace atomic absorption spectroscopy

4.0 RESULTS

4.1 GENERAL DATA

Determined values for pH, nutrients, alkalinity and chloride ion concentration are depicted in Table 4.1.

The pH data are reasonably uniform over both sites, Hidden Bay values range from 5.56 to 6.3 and Quirke Lake range from 5.76 to 6.5. Site HB-1 and HB-2 are slightly lower than the rest of these samples indicating acidic input from the mine effluent stream. However, this represents only a small change and no other systematic variability was observed. In Quirke Lake samples, the reverse was the case with input water being marginally higher than the receiving waters. While no surface trend in pH values could be observed, there was a significant decrease with depth for Quirke Lake indicating that the water column was reasonably stable. Decrease in pH with depth is not surprising as the lake was previously more acidic and present interstitial waters were in the pH 2-5 range, see Table 4.7.

Nutrient data showed considerable variability, but both locations were characterized by low phosphate values. In Hidden Bay, the mine effluent input appeared to be rich in sulphate, but lake values of between 8 and 17 ppm sulphate were observed. In the Quirke Lake samples on the other hand, the input water was significantly lower than that in Hidden Bay but lake values (186-247 ppm) were higher. These data could be explained in terms of the mining history of both areas. Hidden Bay is near a relatively recent, and presently operating mine, whereas the Quirke Lake site is close to a more extensively mined area.

The alkalinity data show that the Hidden Bay samples have considerably more buffering capacity than the Quirke Lake samples, while chloride data show higher concentrations in Quirke Lake. These data impinge on the ionic strength of the two lake waters and are reflected in the calculated model (See Section 5).

Table 4.1 Concentration of Selected Chemical Parameters in Lake Water Samples from Hidden Bay and Quirke Lake

Sample ID*	pH	NO_2/NO_3 ug-at/L (N)	PO_4 ug-at/L (P)	Si ug-at/L (Si)	SO_4 ppm	$CaCO_3$ ppm	Cl ppm
HB-1-0.5	5.56	143.6	0.29	3.38	2463.5	1.30	35.6
HB-2-0.5	5.66	49.1	0.07	7.49	335.5	3.80	8.6
HB-3-1	5.95	64.8	0.06	9.10	16.9	8.70	0.4
HB-4-1	6.10	86.3	0.12	8.01	11.7	7.10	1.1
HB-4-3	6.10	20.1	0.10	2.80	8.0	9.50	0.9
HB-5-1	6.10	3.2	0.07	8.37	12.7	8.80	0.7
HB-5-4	6.30	5.7	0.09	9.97	12.5	8.50	1.0
HB-6-1	6.10	29.4	0.11	3.35	---	9.90	1.6
HB-7-1	---	131.9	0.09	4.24	13.5	9.00	1.3
QL-1-0.3	6.50	1733.0	0.17	14.98	519.2	4.60	34.0
QL-2-1	5.76	972.0	0.50	11.08	246.7	0.00	10.1
QL-3-1	6.00	721.5	0.10	6.32	204.5	2.50	6.8
QL-3-4	6.50	595.5	0.10	10.22	211.0	0.26	10.7
QL-4-1	5.90	1606.0	0.30	0.64	193.5	0.54	12.1
QL-4-8	6.30	677.5	0.20	1.68	185.9	0.80	14.7
QL-4-27	5.60	746.5	0.11	0.43	193.5	0.82	14.8
QL-5-1	6.00	699.0	0.29	5.93	210.8	0.82	12.9
QL-5-8	5.90	1250.0	0.17	2.52	202.4	0.82	6.6
QL-5-18	5.90	664.5	0.10	0.92	196.3	2.20	11.7
QL-6-1	6.30	650.6	0.06	3.42	188.2	2.50	12.8
QL-6-25	5.60	768.5	0.10	0.92	195.5	1.10	14.6

* HB (Hidden Bay) or QL (Quirke Lake) - Station number - depth (in metres).

4.2 METAL DATA

4.2.1 Radionuclide Metal Data

The concentrations of radionuclides in samples from Quirke Lake and Hidden Bay are depicted in Table 4.2. These samples were determined at the University of Waterloo under the direction of Dr. Sharma.

Large lead concentrations, at least an order of magnitude higher than other values were found at Station HB1 and HB2. However, these values were not associated with increased concentrations of Pb-210.

In general the radiocation concentrations are greater in Quirke Lake which is most likely in part due to the level of mining activity and the history of this site. Interestingly, the radiocation concentrations in the water column are larger than the sediment interstitial water, suggesting there is no net flux out of the sediment.

In addition to these data, Dr. Sharma's group at Waterloo also performed several experiments to determine stability constants of selected radiocations with fulvic and humic acids. These experiments were performed with commercially available fulvic radium fulvic. Association were investigated at two ionic strengths and at three pH values. The log k' determined are shown below:

Radiocation Fulvic Stability Constants

Element	Ionic Strength	pH	Log k'
Ra	0.1	2	2.78
		4	3.45
		6	4.41
	0.01	2	3.11
		4	3.79
		6	4.78

Table 4.2 Concentration of Radionuclide in Lake Water.

Sample ID*	Pb ug/L	Pb-210 pCi DL = 3 pCi	U ug/L	Ra x 10^{-14} M DL = 3 ± 2 pCi
QL-1	23.6	16.7		2
QL-2	14.2	10.2	73.7	2.2
QL-3	13.5	9.7		0.5
QL-4	13.2	9.5	72.3	1.5
QL-5	19.2	13.8		2.3
QL-6	13.2	9.3	178	2.3
HB-1	432.0	<		8
HB-2	100.7	<		1.2
HB-3	7.3	<		2.2
HB-4	4.2	<	13.9	1.9
HB-5	5.5	<	5.25	3
HB-6	23.3	<		<
HB-7	5.4	<	3.41	<
QL-1P	21.5	<		<
QL-2P			7.87	<
QL-5P	13.0	<		<
HB-1P	5.2	<		<
HB-2P			0.69	<
HB-5P	7.9	<	0.118	<
HB-6P			<	<
HB-7P			<	<

< indicates less than detection limit

P indicates pore water samples

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Table 4.3 Copper Concentrations from Hidden Bay and Quirke Lake Waters

Sample I.D.*	Total	Inorganic ug/L	Low M.W. ug/L	Organic Bound Metal ug/L[2]	% Organically Bound
HB-1-0.5	1.38	0.63	0.51	0.9	65
HB-2-0.5	0.82	0.11	0.14	0.7	85
HB-3-1		0.22	--		
HB-4-1	0.13	<0.10	<0.10		
HB-4-3		<DL†	<0.10		
HB-5-1		<0.10	<0.10		
HB-5-4		<0.10	<0.10		
HB-6-1		<0.10	<0.10		
HB-7-1		<0.10	<0.10		
QL-1-0.3	0.60	0.56	0.48	0.1	17
QL-2-1		0.26	--		
QL-3-1		0.97	1.00		
QL-3-4		0.76	0.78		
QL-4-1		0.96	0.84		
QL-4-8		0.96	0.94		
QL-4-27		1.10	1.12		
QL-5-1	1.05	0.95	0.85	0.2	19
QL-5-8	0.98	0.90	0.87	0.1	10
QL-5-18		1.16	1.19		
QL-6-1		1.19	0.82		
QL-6-25		1.19	1.03		

* HB (Hidden Bay) or QL (Quirke Lake) - station number - depth (in metres)

† Less than detection limit

D_L = 0.1 based on 3x the blank

[2] All values are to within 0.1

Table 4.4 Zinc Concentrations from Hidden Bay and Quirke Lake Waters

Sample I.D.*	Total Metal ug/L	Inorganic Metal ug/L	Low M.W. Metal ug/L	Organic Metal ug/L[1]	% Organically Bound
HB-1-0.5	4.26	(4.90[2])	(7.40[2])	0.0	0
HB-2-0.5	6.16	0.90	1.00	5.6	91
HB-3-1		<DL†	--		
HB-4-1	<DL	<DL	0.10		
HB-4-3		0.80	0.90		
HB-5-1		0.90	<DL		
HB-5-4		<DL	1.40		
HB-6-1		<DL	1.30		
HB-7-1		3.30	4.10		
QL-1-0.3	8.62	(8.80[2])	(10.50[2])	0	
0					
QL-2-1		2.20	--		
QL-3-1		10.80	12.90		
QL-3-4		9.50	10.20		
QL-4-1		10.70	11.30		
QL-4-8		12.00	12.80		
QL-4-27		9.70	12.60		
QL-5-1	8.96	(9.80[2])	(11.70[2])	0	0
QL-5-8	13.44	11.60	11.90	1.5	11
QL-5-18		10.90	13.20		
QL-6-1		11.90	11.20		
QL-6-25		12.90	11.60		

* HB (Hidden Bay) or QL (Quirke Lake) - station number - depth (in metres)

† Less than detection limit.

0.2 ppb = Detection Limit = 0.2 ppb at 3 x of blank

1 All values ± 0.2

2 Inorganic and low m.w. metal are greater than total. This is due to experimental error and suspected contamination respectively (see text).

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In addition to this experimental data, Dr. Sharma also helped us in obtaining values from the literature. As a result of this effort, good estimates of stability constants could be used in calibration of our model.

4.2.2 Non Radioactive Trace Metal Data

The determined concentrations of trace metals are depicted in Tables 4.3, 4.4, 4.5 and 4.6. For copper, zinc and iron, three operationally defined separations of chemical forms have been attempted. The concentrations tabled as total were determined by filtration (0.45 um) and photo-oxidation by ultra violet radiation using a 1 kw mercury vapour lamp for three hours, prior to Chelex concentration. Photo oxidation breaks the organic C-C bond by free radical attack with hydrogen peroxide. Once the organics have been destroyed, the remaining metal can only be in inorganic complexes or in the free ion form. Most natural water colloids are stabalized by organic films and this process also liberates metal colloids. The chelex concentration procedure doesn't remove metal organic complexes of high stability or colloidally bound metal. The pretreatment described above thus liberates these metal fractions for detection. Accordingly, the total metal concentration described in the tables represent total dissolved metal. Samples that were filtered and then directly concentrated on Chelex-100 have been termed the inorganic fraction. This operationally defined form potentially also includes weakly associated organically bound metals which become dissociated in completion with the Chelex-100 binding sites. In addition positively charged colloidal material may be adsorbed on the column and some colloids will be physically bound to the top of the chelex. The elution step involves 2N acid and the metals associated with these forms will also be included. However, organically and colloidally bound metals represent a small fraction of this total and by far the largest component is inorganic metal complexes and free metal ions.

Those metals determined after ultrafiltration have been termed low molecular weight associated metal. This operationally defined metal

Table 4.5 Iron Concentrations from Hidden Bay and Quirke Lake Waters.

Sample I.D.*	Total Metal ug/L[1]	Inorganic Metal ug/L[1]	Low M.W. Metal ug/L[1]	Organic Metal	% Organically Bound
HB-1-0.5	18.0	18.7	18.3	0.0	0
HB-2-0.5	13.3	10.10	10.30	3.0	23
HB-3-1		<3.0	--		
HB-4-1	2.7	<3.0	<DL†	2.7	0
HB-4-3		<3.0	<DL		
HB-5-1		<3.0	<DL		
HB-5-4		<3.0	0.20<DL		
HB-6-1		<3.0	0.60<DL		
HB-7-1		<3.0	0.30<DL		
QL-1-0.3	35	16.20	<DL	3.2	9
QL-2-1		<3.0	--		
QL-3-1		<3.0	3.30		
QL-3-4		<3.0	0.50<DL		
QL-4-1		<3.0	0.40<DL		
QL-4-8		<3.0	0.40<DL		
QL-4-27		8.90	10.60		
QL-5-1	8.7	5.70	3.20	5.5	63
QL-5-8		<3.0	0.40<DL	-	0
QL-5-18		5.40	10.60		
QL-6-1		<3.0	0.20<DL		
QL-6-25		6.30	3.90		

* HB (Hidden Bay) or QL (Quirke Lake) - station number - depth (in metres).

† Less than detection limit.

<3.0 = Detection Limit = 3 ppb at 3 x of blank.

1 All data ± 3 ppb

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portion includes any metal complexes that may pass through the 1,000 nominal molecular weight ultra filters. This fraction is essentially the same as the inorganic fraction with the exception that weak organic complexes of metals that do not pass through the ultrafilter are not included.

Copper speciation determinations show that considerably more copper is organically bound in the Hidden Bay area than in Quirke Lake. This is probably due to the different pH of each locality and also the known potential input of humus material in the Hidden Bay area.

Similar results are described with zinc but these are much less conclusive as the small number of data points are further reduced by samples at the limit of detection and also by possible contamination of the ultrafiltered samples. Some calibrations have been done to investigate this problem and is explained in Section 4.5. Zn standards put through the ultrafiltration system showed a 1.12% increase. Manipulation of the low M.W. metals data may be in order to correct for this problem. The data presented in Table 4.4 has not been manipulated to allow for this problem.

The iron data presented in Table 4.5 are somewhat variable and significant problems exist in the determination of total iron. Standards show recoveries as low as 50% in some cases and the initial determinations were inadvertantly performed with an old standard which, on subsequent investigation, give erratic results apparently due to particulate formation. Accordingly the totals represent estimates as do numbers calculated using these values. Despite these problems the limited data available shows iron may be up to 65% bound to organic ligands. With these data, distinctions of the two geographical areas is difficult and this may be due to the poor quality of these data.

4.3 ORGANIC DATA

Dissolved organic carbon (DOC), particulate carbon/nitrogen, non-adsorbed organics and adsorbed organic concentrations are given in Table 4.6.

Humic substances in natural waters occur as a continuum, ranging from dissolved, through colloidal, to particulate matter. The dissolved phase is generally the predominant phase (Malcolm, 1985). Separation of dissolved and particulate humic substances is achieved by 0.45 um filtration. Acidification of the filtered water to pH 2 followed by extraction using an XAD-2 resin generally results in the removal of approximately 50% of the dissolved organic carbon (DOC). This is operationally defined as the fraction of dissolved humic substances. In most fresh waters, aquatic humic acids (the fraction of aquatic humic substances which precipitate at pH 1) make up less than 10% of the total humic substances. Thus, approximately 90% of fresh water humic substances are aquatic fulvic acids.

Elemental analysis of fresh water fulvic acids indicates a carbon content of 50-55% by weight. Number average (M_n) molecular weights of fresh water fulvic acids range from 650 - 950 (Malcolm, 1985). For ease of calculation, values of 50% C and M_n = 1000 are widely used (Gillam, pers. comm., 1986).

Thus the fraction adsorbed to the XAD-2 resin can be regarded as the fulvic acid fraction. Calculated molar concentrations of acid are given in Table 4.6.

Relatively few data for XAD-extractable humic substances exist, but from these data an average percent fulvic acid (FA) can be determined. With the exclusion of station QL-5-1, whose value seems somewhat low, the mean percent FA = 50.9 which is within previous determined values.

DOC data showed no obvious trends between sites with the possible exception that average concentrations of DOC were larger in Hidden Bay (3.6 mg C L^{-1}) than in Quirke Lake (2.0 mg C L^{-1}). However, this difference alone could not account for the variation observed in organically bound copper.

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Table 4.6 Organic Concentrations From Hidden Bay and Quirke Lake Water Samples

Sample I.D.*	D.O.C. mg C/L	C:N Ratio	Non-Extractable Dissolved Organic Material mg C/L	XAD-Extractable Humic Substances mg C/L	% FA
HB-1-0.5	7.0	6.9	3.9	2.9	38.4
HB-2-0.5	4.7	6.7	---	---	
HB-3-1	2.2	6.7	0.8	1.4	57.3
HB-4-1	3.3	6.8	---	---	
HB-4-3	3.8	6.9	---	---	
HB-5-1	3.8	6.9	---	---	
HB-5-4	3.2	7.1	---	---	
HB-6-1	3.5	7.1	2.0	1.5	38.6
HB-7-1	1.1	7.0	---	---	
QL-1-0.3	1.1	9.1	---	---	
QL-2-1	1.6	---	0.3	0.8	65
QL-3-1	1.3	9.0	---	---	
QL-3-4	1.3	8.7	0.5	0.8	55.4
QL-4-1	0.8	8.7	---	---	
QL-4-8	2.0	8.9	---	---	
QL-4-27	0.7	9.2	---	---	
QL-5-1	3.6	8.8	2.9	0.7	17.5
QL-5-8	3.5	8.6	---	---	
QL-5-18	1.3	---	---	---	
QL-6-1	3.3	---	---	---	
QL-6-25	3.4	---	---	---	

* HB (Hidden Bay) or QL (Quirke Lake) - station number - depth (in metres).

Carbon to nitrogen ratios were also different in Hidden Bay and Quirke Lake. The low ratios found in Hidden Bay indicate that more biological particulate matter is present (Peters et al., 1978; Riley and Skirrow, 1975). Typical values for particulate with a negligible biological component are approximately 9.0-9.5, thus, Quirke Lake would appear to be devoid of this input mechanism. The biological imput in Hidden Bay may well be responsible for producing metal ligands (other than fulvic) that account for the higher percentage of organic copper binding which was observed.

4.4 INORGANIC CONSTITUENTS IN INTERSTITIAL WATERS

The data for interstitial waters of sediments collected from Hidden Bay and Quirke Lake are presented in Tables 4.7 and 4.8. The data presented in Table 4.7 were determined by Cantest Laboratories. For quality control, blind replicates and blind standards were introduced. These are explained more completely in Section 4.5. The replicate samples shown at the bottom of the table demonstrate that pH, nitrate, phosphate and sulphate results were within 10%. However, nitrate and silicate are more variable. With our model and at acid pH's the association of radiocations with these nutrient elements is of less consequence to the total mobility of these constituents than are organic ligand associations. Average values for the Quirke Lake and Hidden Bay areas were calculated and these were used in our model. These average values are given in Section 5.

Trace metal data are presented in Table 4.8. These data are limited but are sufficient to give us average concentrations for these elements in the interstitial waters of both Quirke Lake and Hidden Bay. Of most significance to the speciation and, hence, mobility of ions in interstitial waters, are the pH and the E_h of solutions. pH measurements have been determined accurately and E_h can be determined from Redox coupled reactions. In our model however, these have not been considered directly, but ranges from oxic to anoxic sediment conditions have been considered. Hidden Bay samples show elevated levels of sulphate as compared to Quirke

Table 4.7 Interstitial Water Concentrations Of Selected Components.

Sample	pH	Nitrate mg/L	Nitrate/ Nitrite mg/L	Phosphate mg/L	Silicate mg/L	Sulphate mg/L
Blank	3.10	<0.1[1]	8.90	<0.06	<0.08	0.10
Blank	2.62	<1	73.0	<0.06	0.34	<0.6
HB1	2.60	<3	94.0	<2.0	1.16	2990
HB2	1.77	<3	1600	<2.0	2.12	2800
HB3	4.36	<3	13.00	<2.0	5.80	130
HB4	2.18	<3	180	<2.0	0.81	2200
HB7	2.91	<1	28.0	<0.6	0.08	8.8
QL-1	2.60	<1	130.0	<0.6	<0.08	370
QL-2	3.20	<1	50.0	<0.6	<0.08	145
QL-3	5.31	<1	9.5	<0.6	10.5	150
QL-4	3.87	<1	12.0	<0.6	1.01	145
QL-5	2.24	<1	400	<0.6	0.16	110
Repeats						
HB1	2.70	<1	70	<0.6	0.67	2870
HB7	2.91	<0.5	33	<0.03	0.31	11.0

[1] < values indicate analytical limits of detection.

Table 4.8 Interstitial Water Trace Metal Concentrations

Sample I.D.*	Copper ug/L	Zinc ug/L	Iron ug/L	Lead ug/L	Uranium ug/L	Radium ug/L
HB-1	0.91	850	1370	5.2		<0.1
HB-2	9.31	5520	2830		0.69	<0.1
HB-3				7.9	0.118	<0.1
HB-4					<	<0.1
HB-7					<	<0.1
QL-1	8.48	2300	131	21.5		<0.1
QL-2					7.87	<0.1
QL-3	1.44	1180	18.9			<0.1
QL-5	3.80	3600	650	13.0		<0.1

* HB (Hidden Bay) or QL (Quirke Lake) - station number - depth (in metres)

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Lake but other nutrient parameters are approximately constant in both environments with the exception of elevated nitrate/nitrite concentrations at Hidden Bay site 2. Only limited trace metal numbers were determined and these were only for ionic metal concentrations referred to as inorganically bound in the previous section.

In addition to copper, iron and zinc; lead, uranium and radium were determined at the University of Waterloo. Six data points were contracted and a selection was received. However, these data are sufficient in order to make a first approximation with our model. Because we have no direct speciation values for these metals in interstitial waters, the fine-tuning of our model is not possible. However, adjustments performed under Section 5 to fit environmental data to our model were successful for the dissolved water speciation and the same model can be used for interstitial waters. Average concentrations for iron in Hidden Bay are considerably larger than in the Quirke Lake site. Both copper and zinc are similar at both sites. Lead has a reverse trend with high levels existing in Quirke Lake as does uranium. All radium data were less than detection limit and have been included in the model at an estimated concentration.

4.5 QUALITY CONTROL

All analyses were carried out by qualified chemists using standard operating procedures and reliable, well maintained equipment. All operations were closely supervised to ensure that procedures such as sample documentation, sub-sampling, equipment calibration, sample replication, data recording and data processing were strictly adhered to. All glassware and plasticware used for the analyses was either acid washed (trace metals and nutrients) or baked at 500°C (DOC) to remove contaminants.

Alkalinity standardization was performed in triplicate each day and samples were run in duplicate. Standard buffer solutions were used to calibrate the pH meter. Standardization for chloride analyses was also performed in triplicate and three blanks were run each day. Results were blank corrected.

Nutrient stock standard solutions were calibrated using Sagami standards of known nutrient content. Calibration standards for the automated analyses were prepared fresh daily and run after every 20 samples in order to correct for instrumental drift. Blank correction was not required as the Milli-Q deionized water used in standards and wash solutions did not contain measurable amounts of analyte.

All dissolved organic carbon analyses were run in duplicate and blank corrected.

Blank corrections were also applied to the Chelex, XAD resin and ultrafiltration separations where necessary.

The graphite furnace AA analyses were all performed in duplicate. The working curve was updated after every eight samples by use of a 'reslope' facility built into the programmable autosampler. During 'reslope', the matrix blank and the mid-concentration calibration standard were automatically re-run and the calibration curve was re-established using these points. In addition, calibration standards were run after every six to eight samples in order to provide an instrument drift correction.

For all flame AA analyses the working curve was checked after each sample reading by aspirating a standard of the nearest concentration. If the standard reading had, at my time, drifted outside the expected precision limits for that element the calibration curve was re-entered and the last sample reading was repeated.

All subcontracted analyses were performed with the inclusion of unknown standards and blind replicate samples. In the case of interstitial water analyses performed by Cantest, these were beneficial in showing potential problems with these analyses. Standard values for silicates and sulphates varied by up to 20%, phosphates by 10%. The maximum precision on these analyses appear to be in the order of 10%. Radiocation determinations performed by the University of Waterloo were also sent with blind replicate

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samples and some standards. However, due to changes in the terms of the contract and the analyses which were in the end performed, these data were not provided together with the analyses. I am assured by Dr. Sharma that their analyses were accurate to within 1 ug/L for lead and uranium and that radium concentrations are not in excess of 10^{-12} mol, determined values ranging from less than detectable to 8×10^{-14} mol.

From the point of view of the model those values which most greatly affect the speciation of radiocations are, in fact, the determined stability constants. The majority of these stability constants were obtained from the literature and in calibrating the model to environmental data (see Section 5) these stability constants have been changed in order to obtain improved data fit. We are confident that the analyses performed are to within the precisions provided.

5.1 LITERATURE REVIEW

In order that the correct input data could be obtained for our speciation model, concentrations and stability constants of cations and potential ligands were obtained from the literature. Some of the relevant data was obtained from the review performed by Monenco for the National Uranium Tailings Program (Contract No OSQ84-000297). However, the stability constant data for uranium used in our program was obtained from the seven references that appear in Table 5.5, none of which were included in the above review. Additional site specific information of the concentrations of relevant ligands and cations in the Hidden Bay and Quirke Lake areas was obtained largely from the open literature, and our own data. A considerable quantity of information was also obtained from Eldorado Resources Ltd. from work performed for them by the Saskatchewan Geological Survey in 1976. In addition, two confidential reports and a report entitled "An Examination of Water Quality in the Rabbit Lake Drainage Basin" (1984) were used.

Concentration data for lake water from the Quirke Lake area were obtained from both the open literature and through M. A. Vivyurka of Rio Algom Limited. Mr. Vivyurka's cooperation with our field personnel, and with Dobrocky Seatech Ltd. and CANMET personnel in the provision of chemical concentration data was much appreciated and has meant that sufficient data for our model was obtained expediently.

Details of the references used are given in Section 5.2

5.2 DESCRIPTION OF COMPUTER PROGRAM

The computer program MINEQL and accompanying data files were acquired from the Massachusetts Institute of Technology and the University of Victoria. This acquired version had been modified from the original version of MINEQL[1], such that the ionic strength of the solution was an input parameter rather than a fixed value. Other minor modifications were those necessary to be compatible with the University of Victoria computer.

MINEQL is a FORTRAN program which calculates equilibrium concentrations of species in aqueous solution. The calculation takes into account the precipitation and/or dissolution of solids and redox reactions. MINEQL consists of the main program and two data files.

The main program is divided into two parts. The first part MINEQL consists of the main program which initializes the parameters ITMAX, THRSH and EPS and calls the subroutines needed to solve the problem (See Table 5.1 for description of variables). This is referred to as MAIN in the documentation. The program MINSUB consists of all the subroutine programs. A flow chart of MINEQL is presented in Table 5.2, as well as storage requirements. The data file THRM contains the thermodynamic data on both soluble and solid complexes formed by the components. The data includes the logarithm of the formation constant and stoichiometry of the complex. The formation constants used are those determined at zero ionic strength and 25°C.

This data file has been updated to include as much thermodynamic data as possible on complexes formed by UO_2^{+2}, U^{+4}, U^{+2}, Th^{+4} and Ra^{+2}, as well as complexes of these elements and other trace metals with fulvic acid. To date, there are approximately 1500 stability constants in the THRM file. The program is capable of handling up to 200 components; 100 cations (metals) and 100 anions (ligands). Currently only 96 components are on file, thus there is ample room for the addition of components of interest.

A list of all the components now incorporated into this program is presented in Appendix 1. The data file IONC contains charge information on each component which is used in the ionic strength correction calculation.

The input data required to run MINEQL are the ionic strength of the solution and the molar concentration of each component in solution. The equilibrium speciation of a solution is most fully described if the concentrations of all the components in the solution are known. The

Table 5.1 Description of Principle Variables

A(I,J,)	-	the stoichiometric coefficient of component J in species I
C(I)	-	the concentration of species (I)
EPS	-	the tolerance in the convergence test (EPS = 10^{-4} is a convenient value)
GC(I)	-	the $\log_{10}$ of C(I)
GK(I)	-	the $\log_{10}$ of the stability constant for species I
GX(J)	-	the $\log_{10}$ of X(J)
IDX(J)	-	the identification number of component J
IDY(I)	-	the identification number of species I
ITMAX	-	the maximum number of iterations allowed for a problem (for a single case ITMAX = 40 is usually sufficient to achieve convergence, if the problem is to converge at all)
ITER	-	the counter for number of iterations
NN(L)	-	the number of species of type L
NXDIM	-	the X (component) dimension of the arrays
NYDIM	-	The Y (species) dimension of the arrays
T(J)	-	analytical (total) concentration of component J
THRSH	-	threshold for percentage distribution output (THRSH = 0.01, 1% is a convenient value)
X(J)	-	concentration of component J
XMU	-	ionic strength
Y(J)	-	the remainder in the mass balance equation for component J
Z(J,K)	-	the element of the Jacobian representing Y_J / X_K

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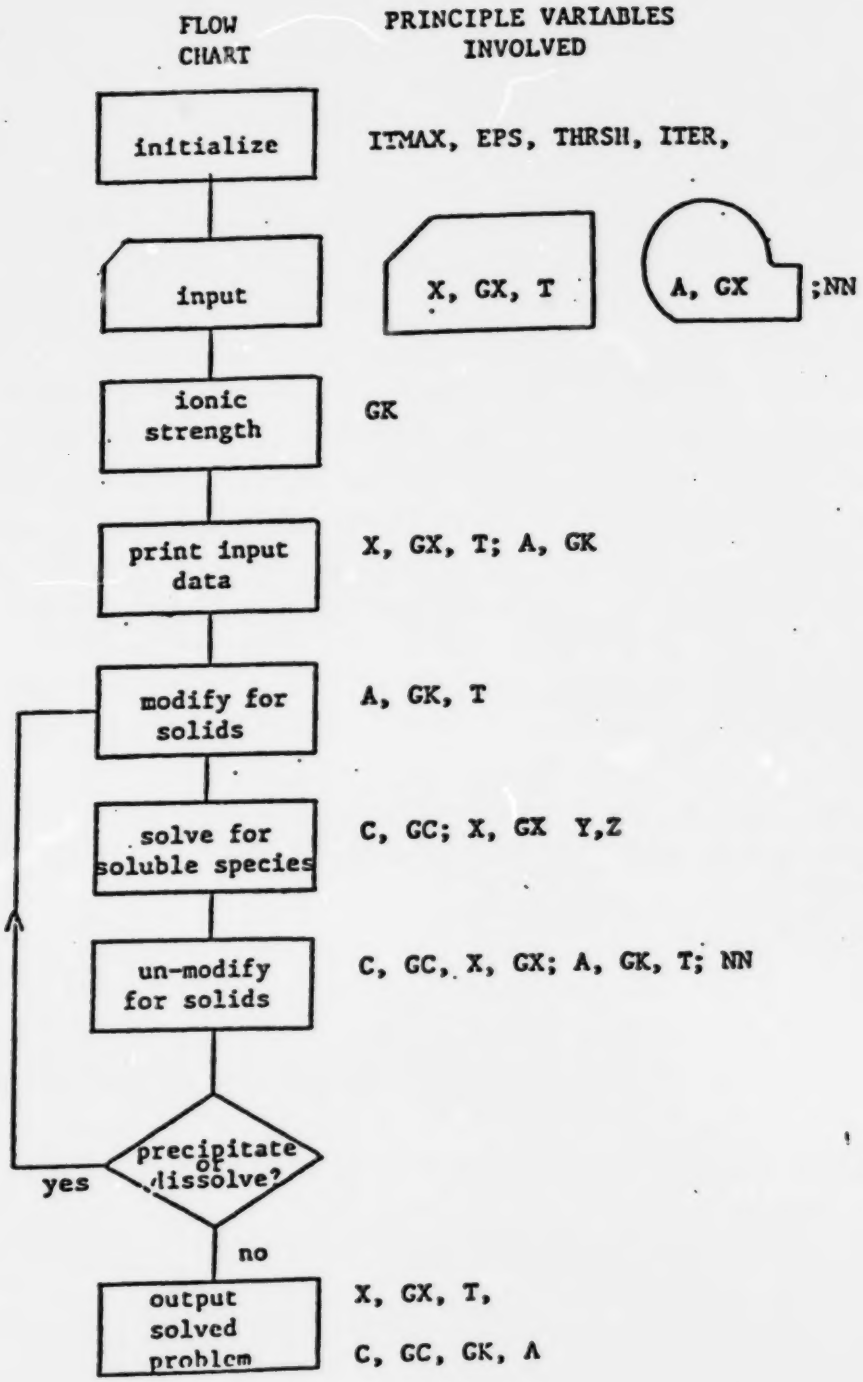
Table 5.2 Flow Chart of MINEQL FORTRAN



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program combines the input data with the thermodynamic data for all the species formed from the components. An ionic strength correction is performed on the data. The program then attempts to solve for the soluble species, making the necessary modifications for the presence of solid phases, until a solution is found.

As input information, it is possible to make modifications or place constraints on the calculations, such as fixing the concentration of a component or complex, not allowing the dissolution of a solid, ignoring the presence of a particular complex, or changing a constant from its data file value.

The final solution presents each complex as a percentage of the total concentration of the component. The concentration of each complex is included in the intermediate output. An example of such an output is shown in Appendix 2.

5.3 CREATION OF DATA FILES

A data file for each sample collected was created. The code name for the same was the name used for the data file (see Table 5.3). Each file consists of:

a) title;

b) ionic strength;

and c) water composition data.

The title for each file is the location, site number and site depth.

Ionic strength is calculated individually for each site using the components present in highest concentration, according to the following equation:

$$U = 1/2 \ \Sigma \ C_i \ Z_i^2$$

U = ionic strength

C_i = concentration of i^{th} component

Z_i = charge of i^{th} component

values followed by an * indicate values used in ionic strength calculation.

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Table 5.3 Data Files

HIDDEN BAY SITE 1 - DEPTH 0.5 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	9.87E-6
Zn^{+2}	7.50E-5
FA	
Fe^{+3}	3.35E-3
UO_2^{+2}	4.00E-8
H^+	2.80E-6
CO_3^{-2}	1.30E-5
Cl^-	1.00E-3
SO_4^{-2}	2.51E-2
PO_4^{-3}	9.28E-9
NO_3^-	1.03E-5
$SiO_2(OH)_2$	1.20E-7
pH	5.56
pE	

HIDDEN BAY SITE 2 - DEPTH 0.5 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.76E-6
Zn^{+2}	1.38E-5
FA	
Fe^{+3}	1.80E-4
UO_2^{+2}	
H^+	2.19E-6
CO_3^{-2}	3.80E-5
Cl^-	2.40E-4
SO_4^{-2}	3.41E-3
PO_4^{-3}	2.31E-9
NO_3^-	3.51E-6
$SiO_2(OH)_2$	2.66E-7
pH	5.66
pE	1.27

HIDDEN BAY SITE 3 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	3.51E-6
Zn^{+2}	4.60E-6
FA	1.48E-6
Fe^{+3}	7.16E-6
UO_2^{+2}	4.20E-8
H^+	1.12E-6
CO_3^{-2}	8.70E-5
Cl^-	1.00E-5
SO_4^{-2}	1.72E-4
PO_4^{-3}	1.88E-9
NO_3^-	4.63E-6
$SiO_2(OH)_2$	3.24E-7
pH	5.95
pE	

HIDDEN BAY SITE 4 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	8.34E-7
Zn^{+2}	4.60E-6
FA	
Fe^{+3}	1.79E-5
UO_2^{+2}	
H^+	7.94E-7
CO_3^{-2}	7.10E-5
Cl^-	3.10E-5
SO_4^{-2}	1.19E-4
PO_4^{-3}	4.03E-9
NO_3^-	6.17E-6
$SiO_2(OH)_2$	2.85E-7
pH	6.10
pE	0.68

Table 5.3 Data Files (continued)

HIDDEN BAY SITE 4 - DEPTH 3 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	8.18E-7
Zn^{+2}	1.22E-5
FA	
Fe^{+3}	5.37E-6
UO_2^{+2}	4.00E-8
H^+	7.90E-7
Fe^{+2}	0.00E-6
Cu^+	0.00E-6
CO_3^{-3}	9.50E-5
Cl^-	2.50E-5
SO_4^{-2}	8.15E-5
PO_4^{-3}	3.08E-9
NO_3^-	1.44E-6
$SiO_2(OH)_2$	9.95E-8
pH	6.10
pE	5.00

HIDDEN BAY SITE 5 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	6.29E-7
Zn^{+2}	1.38E-5
FA	
Fe^{+3}	1.61E-5
UO_2^{+2}	
H^+	7.94E-7
Fe^{+2}	
Cu^+	
CO_3^{-2}	8.80E-5
Cl^-	2.00E-5
SO_4^{-2}	1.29E-4
PO_4^{-3}	2.40E-9
NO_3^-	2.31E-7
$SiO_2(OH)_2$	2.98E-7
pH	6.10
pE	1.19

HIDDEN BAY SITE 5 - DEPTH 4 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.95E-6
Zn^{+2}	4.60E-6
FA	
Fe^{+3}	7.16E-6
UO_2^{+2}	
H^+	5.01E-7
CO_3^{-2}	8.50E-5
Cl^-	2.80E-5
SO_4^{-2}	1.27E-4
PO_4^{-3}	2.95E-9
NO_3^-	4.07E-7
$SiO_2(OH)_2$	3.55E-7
pH	6.30
pE	1.69

HIDDEN BAY SITE 6 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	9.44E-7
Zn^{+2}	4.60E-6
FA	
Fe^{+3}	2.15E-5
UO_2^{+2}	
H^+	7.94E-7
CO_3^{-2}	9.90E-5
Cl^-	4.50E-5
SO_4^{-2}	1.92E-3
PO_4^{-3}	3.42E-9
NO_3^-	2.10E-6
$SiO_2(OH)_2$	1.19E-7
pH	6.10
pE	0.85

Table 5.3 Data Files (continued)

HIDDEN BAY SITE 7 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.98E-6
Zn^{+2}	5.05E-5
Fe^{+3}	7.16E-6
UO_2^{+2}	
H^+	
CO_3^{-2}	9.00E-5
Cl^-	3.70E-5
SO_4^{-2}	1.37-4E-4
PO_4^{-3}	2.95E-9
NO_3^-	9.42E-6
$SiO_2(OH)_2$	1.51E-7
pH	
pE	

QUIRKE LAKE SITE 1 - DEPTH 0.3 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	8.80E-6
Zn^{+2}	1.34E-4
Fe^{+3}	2.90E-4
UO_2^{+2}	
H^+	3.16E-7
CO_3^{-2}	4.60E-5
Cl^-	9.60E-4
SO_4^{-2}	5.29E-3
PO_4^{-3}	5.57E-9
NO_3^-	1.23E-4
$SiO_2(OH)_2$	5.33E-7
pH	6.50
pE	2.03

QUIRKE LAKE SITE 2 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	4.06E-6
Zn^{+2}	3.36E-5
Fe^{+3}	2.15E-5
UO_2^{+2}	
H^+	1.74E-6
CO_3^{-2}	
Cl^-	2.85E-4
SO_4^{-2}	2.51E-3
PO_4^{-3}	1.61E-8
NO_3^-	6.94E-5
$SiO_2(OH)_2$	3.94E-7
pH	5.76
pE	1.95

QUIRKE LAKE SITE 3 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.53E-5
Zn^{+2}	1.65E-4
Fe^{+3}	4.83E-5
UO_2^{+2}	
H^+	1.00E-6
CO_3^{-2}	2.50E-5
Cl^-	1.90E-4
SO_4^{-2}	2.08E-3
PO_4^{-3}	3.08E-9
NO_3^-	5.15E-5
$SiO_2(OH)_2$	2.25E-7
pH	6.00
pE	2.54

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Table 5.3 Data Files (continued)

QUIRKE LAKE SITE 3 - DEPTH 4 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.19E-5
Zn^{+2}	1.45E-4
Fe^{+3}	1.79E-5
UO_2^{+2}	
H^+	3.16E-7
CO_3^{-2}	2.60E-6
Cl^-	3.41E-4
SO_4^{-2}	2.15E-4
PO_4^{-3}	3.17E-9
NO_3^-	4.25E-5
$SiO_2(OH)_2$	3.63E-7
pH	6.50
pE	3.22

QUIRKE LAKE SITE 4 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.15E-5
Zn^{+2}	1.64E-4
Fe^{+3}	1.07E-5
UO_2^{+2}	
H^+	1.26E-6
CO_3^{-2}	5.40E-6
Cl^-	4.15E-4
SO_4^{-2}	1.97E-3
PO_4^{-3}	9.58E-9
NO_3^-	1.15E-4
$SiO_2(OH)_2$	2.27E-8
pH	5.90
pE	2.54

QUIRKE LAKE SITE 4 - DEPTH 8 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.51E-5
Zn^{+2}	1.83E-4
Fe^{+3}	8.95E-6
UO_2^{+2}	
H^+	5.01E-7
CO_3^{-2}	8.00E-6
Cl^-	4.17E-4
SO_4^{-2}	1.89E-3
PO_4^{-3}	6.57E-9
NO_3^-	4.84E-5
$SiO_2(OH)_2$	5.98E-7
pH	6.30
pE	2.20

QUIRKE LAKE SITE 4 - DEPTH 27 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.74E-5
Zn^{+2}	1.48E-4
Fe^{+3}	1.59E-4
UO_2^{+2}	
H^+	2.51E-6
CO_3^{-2}	8.20E-6
Cl^-	3.63E-4
SO_4^{-2}	1.97E-3
PO_4^{-3}	3.65E-9
NO_3^-	5.33E-5
$SiO_2(OH)_2$	1.52E-8
pH	5.60
pE	2.54

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Table 5.3 Data Files (continued)

QUIRKE LAKE SITE 5 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.50E-5
Zn^{+2}	1.50E-4
Fe^{+3}	1.02E-4
UO_2^{+2}	
H^+	1.00E-6
CO_3^{-2}	8.20E-6
Cl^-	1.87E-4
SO_4^{-2}	2.15E-3
PO_4^{-3}	9.41E-9
NO_3^-	4.99E-5
$SiO_2(OH)_2$	2.11E-7
pH	6.00
pE	2.37

QUIRKE LAKE SITE 5 - DEPTH 8 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.46E-5
Zn^{+2}	1.77E-4
Fe^{+3}	1.79E-5
UO_2^{+2}	
H^+	1.26E-6
CO_3^{-2}	8.20E-6
Cl^-	3.30E-4
SO_4^{-2}	2.06E-3
PO_4^{-3}	5.40E-9
NO_3^-	8.93E-5
$SiO_2(OH)_2$	8.96E-8
pH	5.90
pE	2.37

QUIRKE LAKE SITE 5 - DEPTH 18 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.51E-5
Zn^{+2}	1.83E-4
Fe^{+3}	8.95E-6
UO_2^{+2}	
H^+	5.01E-7
CO_3^{-2}	8.00E-6
Cl^-	4.17E-4
SO_4^{-2}	1.89E-3
PO_4^{-3}	6.57E-9
NO_3^-	4.84E-5
$SiO_2(OH)_2$	5.98E-7
pH	6.30
pE	2.20

QUIRKE LAKE SITE 6 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.87E-5
Zn^{+2}	1.82E-4
Fe^{+3}	4.66E-5
UO_2^{+2}	
H^+	5.01E-7
CO_3^{-2}	2.51E-5
Cl^-	4.82E-4
SO_4^{-2}	1.99E-3
PO_4^{-3}	3.88E-9
NO_3^-	4.65E-5
$SiO_2(OH)_2$	1.22E-7
pH	6.30
pE	1.53

Table 5.3 Data Files (continued)

QUIRKE LAKE SITE 5 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.50E-5
Zn^{+2}	1.50E-4
Fe^{+3}	1.02E-4
UO_2^{+2}	
H^+	1.00E-6
CO_3^{-2}	8.20E-6
Cl^-	1.87E-4
SO_4^{-2}	2.15E-3
PO_4^{-3}	9.41E-9
NO_3^-	4.99E-5
$SiO_2(OH)_2$	2.11E-7
pH	6.00
pE	2.37

QUIRKE LAKE SITE 5 - DEPTH 8 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.46E-5
Zn^{+2}	1.77E-4
Fe^{+3}	1.79E-5
UO_2^{+2}	
H^+	1.26E-6
CO_3^{-2}	8.20E-6
Cl^-	3.30E-4
SO_4^{-2}	2.06E-3
PO_4^{-3}	5.40E-9
NO_3^-	8.93E-5
$SiO_2(OH)_2$	8.96E-8
pH	5.90
pE	2.37

QUIRKE LAKE SITE 5 - DEPTH 18 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.51E-5
Zn^{+2}	1.83E-4
Fe^{+3}	8.95E-6
UO_2^{+2}	
H^+	5.01E-7
CO_3^{-2}	8.00E-6
Cl^-	4.17E-4
SO_4^{-2}	1.89E-3
PO_4^{-3}	6.57E-9
NO_3^-	4.84E-5
$SiO_2(OH)_2$	5.98E-7
pH	6.30
pE	2.20

QUIRKE LAKE SITE 6 - DEPTH 1 M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.87E-5
Zn^{+2}	1.82E-4
Fe^{+3}	4.66E-5
UO_2^{+2}	
H^+	5.01E-7
CO_3^{-2}	2.51E-5
Cl^-	4.82E-4
SO_4^{-2}	1.99E-3
PO_4^{-3}	3.88E-9
NO_3^-	4.65E-5
$SiO_2(OH)_2$	1.22E-7
pH	6.30
pE	1.53

Table 5.3 Data Files (continued)

QUIRKE LAKE SITE 6 - DEPTH 25M

Parameter	Concentration ($M.L^{-1}$)
Ionic Strength	
Cu^{+2}	1.88E-5
Zn^{+2}	1.97E-4
Fe^{+3}	1.12E-4
UO_2^{+2}	
H^+	2.51E-6
CO_3^{-2}	1.10E-5
Cl^-	4.12E-4
SO_4^{-2}	1.99E-3
PO_4^{-3}	3.23E-9
NO_3^-	5.49E-5
$SiO_2(OH)_2$	4.00E-8
pH	5.60
pE	2.20

Water composition, as outlined in the document, consists of a code number for the component, initial guess of concentration (log C) and total molar concentration of the component in solution. Analytical data acquired has been converted to molar concentrations using the conversion factors in Table 5.4. The format of the input data is described in Appendix 3.

5.3.1 Augmenting Thermodynamic Data - THRM.DAT

When acquired, MINEQL was accompanied by THRM.DAT, a data file consisting of the stability constants for approximately 1500 possible complexes formed by the components included in the program. The program considers the formation of complexes from the individual components. Thus overall formation constants rather than stepwise formation constants are used in THRM DATA and THRM DAT (see Appendix 1 for further discussion on interpretation of formation constants). The constants which were included in THRM. DAT have not been changed or verified in any way except for the complexes of UO_2^{+2} and Th^{+4} which are of particular interest to this project. Some of the constants for complexes with these elements were changed and others addedin the THRM. DAT file, based on values obtained from the literature. In addition, U^{+4} and Ra^{+2} were introduced as components and appropriate complexes added to the file. The complexation of metals by organic matter was incorporated in the form of the component FA^{-} (fulvic acid), and appropriate stability constants for complexes with Cu^{+2}, Zn^{+2}, $Fe^{+2,+3}$, UO_2^{+2}, and Th^{+} were added to THRM. DAT. The choice of these constants and the references used are shown in Table 5.5.

A summary of the complexes of the radionuclides which are currently in THRM. DAT are given in Table 5.5 with the log of the corresponding formation constants. A tabulation of the literature values accumulated is given with the underlined values being those which were chosen as the THRM. DAT value. The complexes could be added to the data file if it is thought that the calculated speciation does not represent the "real life" situation. An alternative to adding more complexes, is to change the values of log K to one of the other literature values, for major complexes already in the file.

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Table 5.4 Conversion Factors

Sulphate: SO_4^{-2} data is in ppm

M.W. 98.06

$$[SO_4^{=}] = \frac{ppm \times 10^{-3}}{98.1} = M.L^{-1}$$

Alkalinity: data is in ppm $CaCO_3$

M.W. 100.1

$$[CO_3^{=}] = [CaCO_3] = \frac{ppm \times 10^{-3}}{100.1} = M.L^{-1}$$

Chloride: Cl^- data is in ppm

M.W. 35.45

$$[Cl^-] = \frac{ppm \times 10^{-3}}{35.45}$$

Nitrate: NO_3^- data is in ug/l N, assumed all NO_3^-

M.W. of N = 14.0

$$[NO_3^-] = [N] = \frac{ug/l \times 10^{-6}}{14.0} = moles/l$$

Phosphate: PO_4^{-3} data is in ug/l of P, assumed all is as PO_4^{-3}

M.W. of P = 31.0

$$[PO_4^{-3}] = [P] = \frac{ug/l \times 10^{-6}}{31.0} = M.L^{-1}$$

Silicate: SiO_3^{-2} data is ug/l of Si, assumed all is SiO_3

M.W. of Si = 28.1

$$[SiO_3^{-2}] = [Si] = \frac{ug/l \times 10^{-6}}{28.1} = M.L^{-1}$$

Table 5.4 Conversion Factors (continued)

Copper: Cu^{+2} data is in ppm - assume all is Cu^{+2}

M.W. = 63.55

$$[Cu^{+2}] = \frac{ppm \times 10^{-3}}{63.55} = M.L.^{-1}$$

Zinc: Zn^{+2} data is in ppm

M.W. = 65.38

$$[Zn^{+2}] = \frac{ppm \times 10^{-3}}{65.38} = M.L^{-1}$$

Iron: Fe^{+3} data is in ppm - assume all is Fe^{+3}

M.W. = 55.84

$$[Fe^{+3}] = \frac{ppm \times 10^{-3}}{55.84} = M.L^{-1}$$

Conversion of E_h values

$p = -\log$

$E_h = -0.059 \log$ at 25°C E_h in volts

$$\frac{E_h}{-0.059} = \log$$

Conversion of DOC values to molar concentrations of fulvic acid

Failing that:

(1) $$\frac{DOC}{945} = \frac{mg\ C/l \times 10^{-3}}{945} = moles/l\ FA$$

- this assumes DOC is weight g FA, not carbon

HB-1-1	3.07×10^{-6}	QL-1-1	8.47×10^{-7}
HB-3-1	1.48×10^{-6}	QL-3-4	8.47×10^{-7}
HB-6-1	1.59×10^{-6}	QL-5-1	7.41×10^{-7}

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Table 5.4 Conversion Factors (continued)

(OR) (2) A CHN analysis of five samples of Humic acid (commercial) showed 40% C content (on average). If fulvic acid is assumed to be similar, then the weight of carbon in one mole of fulvic acid is 0.40 x 945 = 189 g/ mole.

$$\frac{\text{DOC mg C/l} \times 10^{-3}}{378} = \text{M.L}^{-1}$$

HB-1-1	1.5×10^{-5}	QL-1-1	4.23×10^{-6}
HB-3-1	7.4×10^{-6}	QL-3-4	4.23×10^{-6}
HB-6-1	7.94×10^{-6}	QL-5-1	3.70×10^{-6}

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Table 5.5 Stability Constant Data Used to Modify "THRM. DAT".

	Original THRM DATA	Ref. 1	Ref. 2	Ref. 3	Ref. 4	Ref. 5	Ref. 6	Ref. 7
$UO_2^{+2} + F^- \rightarrow UO_2F^+$	5.10	5.13	5.1					
$UO_2^{+2} + 2F^- \rightarrow UO_2F_2$	8.80	8.94	9.0					
$UO_2^{+2} + 3F^- \rightarrow UO_2F_3^-$	11.40	11.35	11.3					
$UO_2^{+3} + 4F^- \rightarrow UO_2F_4^=$	12.40	12.60	12.6					
$UO_2^{+2} + Cl^- \rightarrow UO_2Cl^+$	0.90	0.21	1.61					
$UO_2^{+2} + BR^- \rightarrow UO_2BR^+$	0.30							
$UO_2^{+2} + NO_3^- \rightarrow UO_2NO_3^+$	-							-0.25
$UO_2^{+2} + NO_3^- \rightarrow UO_2(SO_4)$	3.00	2.71	2.9					
$UO_2^{+2} + 2SO_4^= \rightarrow UO_2(SO_4)_2$	4.60	4.15						
$UO_2^{+2} + H_2O \rightarrow UO_2(OH) + H^+$	-5.3		-5.8	-5.8			-5.5	
$2UO_2^{+2} + 2H_2O \rightarrow (UO_2)_2(OH)_2 + 2H^+$	-		-5.6	-5.6	-5.89		-5.89	
$3UO_2^{+2} + 5H_2O \rightarrow (UO_2)_3(OH)_5 + 5H^+$	-		15.6	-15.6	-16.2		-16.46	
$3UO_2^{+2} + 7H_2O \rightarrow (UO_2)_3(OH)_7 + 7H^+$	-		-31.				-22.76	
$UO_2^{+2} + 2H_2O \rightarrow UO_2(OH)_2 + 2H^+$	-		-12.					
$3UO_2 = 4H_2O \rightarrow (UO_2)_3(OH)_4 + 4H^+$	-						-12.31	
$UO_2^{+2} + CO_3^= \rightarrow UO_2(CO_3)$	-		10.1		9.5			
$UO_2^{+2} + 2CO_3 \rightarrow UO_2(CO_3)_2^=$	16.8	17.0	17.1		16.2	16.6		
$UO_2^{+2} + 3CO_3 \rightarrow UO_2(CO_3)_3^{-4}$	22.7	21.4	21.4		21.8	21.3		
$UO_2^{+2} + 2H^+ + 2PO_4^{-3} \rightarrow UO_2(HPO_4)^=$	-	43.3						
$UO_2^{+2} + H^+ + Si_2O_2(OH_2)^- \rightarrow UO_2Si_1O(OH)_3$	-	20.3						
SOLIDS								
$UO_2^{+2} + CO^{3=} \rightarrow UO_2(CO_3)$	12.90	14.46		14.2		14.4		
$UO_2^{+2} + CO_3^= \rightarrow UO_2(OH)_2$	-5.7			-5.7				
$2UO_2^+ + 2HPO_4^= \rightarrow (UO_2)_2(HPO_4)_2$	-			23.				

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Table 5.5 Stability Constant Data Used to Modify "THRM. DAT" (Continued)

	Original THRM Data	Ref. (1)	Ref. (2)	Ref. (3)
$Th^{+4} + F^- \rightarrow ThF^{+3}$	8.80	8.03	8.44	
$Th^{+4} + 2F^- \rightarrow ThF_2^{+2}$	15.70	14.25	15.06	
$Th^{+4} + 3F^- \rightarrow ThF_3^{+}$	20.80	18.93	19.81	
$Th^{+4} + 4F^- \rightarrow ThF_4$	--	22.31	23.17	
$Th^{+4} + Cl^- \rightarrow ThCl^{+3}$	1.40	1.09		
$Th^{+4} + 2Cl^- \rightarrow ThCl_2^{+2}$	--	0.08		
$Th^{+4} + 3Cl^- \rightarrow ThCl_3^{+}$	--	1.65		
$Th^{+4} + 4Cl^- \rightarrow ThCl_4$	--	1.26		
$Th^{+4} + SO_4^{=} \rightarrow ThSO_4^{+2}$	5.8	5.45		
$Th^{+4} + 2SO_4^{=} \rightarrow Th(SO_4)_2$	9.4	9.73		
$Th^{+4} + 3SO_4^{=} \rightarrow Th(SO_4)_3^{=}$	--	10.50		
$Th^{+4} + 4SO_4^{=} \rightarrow Th(SO_4)_4^{4-}$	--	8.48		
$Th^{+4} + NO_3^- \rightarrow Th(NO_3)^{+3}$	--	0.94		
$Th^{+4} + 2NO_3^- \rightarrow Th(NO_3)_2^{+2}$	--	1.97		
$Th^{+4} + H^+ + PO_4^{-3} \rightarrow Th(HPO_4)^{+2}$	--	23.3		
$Th^{+4} + 2H^+ + 2PO_4^{-3} \rightarrow Th(HPO_4)_2$	--	47.8		
$Th^{+4} + 3H^+ + 3PO_4^{-3} \rightarrow Th(HPO_4)_3$	--	68.8		
$Th^{+4} + 2H^+ + PO_4^{-3} \rightarrow Th(H_2PO_4)^{+3}$	--	28.8		
$Th^{+4} + 3H^+ + PO_4^{-3} \rightarrow Th(H_3PO_4)^{+4}$	--	23.8		
$Th^{+4} + H_2O \rightarrow ThOH^{+3} + H^+$	-2.10	-3.20		-3.20
$Th^{+4} + 2H_2O \rightarrow Th(OH)_2^{+2} + 2H^+$	--	-6.93		-6.93
$Th^{+4} + 3H_2O \rightarrow Th(OH)_3^{+} + 3H^+$	--	(-11.7)		(-11.7)
$Th^{+4} + 4H_2O \rightarrow Th(OH)_4 + 4H^+$	--	-15.9		-15.9
$2Th^{+4} + 2H_2O \rightarrow Th_2(OH)_2^{+6} + 2H^+$				-6.14
$4Th^{+4} + 8H_2O \rightarrow Th_4(OH)_8^{+8} + 8H^+$				-21.1
$6Th^{+4} + 15H_2O \rightarrow Th_6(OH)_{15}^{+9} + 15H^+$				-36.76
SOLIDS				
$Th^{+4} + 4H_2O \rightarrow Th(OH)_4(S) + 4H^+$	-44.4			-46.6

Legend to Table 5.5

1. Longmuir, Donald, 1978. Uranium solution - mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica Acta 42: 547

2. Lemire, R.J. and P.R. Tremaine, 1980. Uranium and plutonium equilibria in aqueous solution to 200°C. J. Chem. Eng. Data 25: 361.

3. Baes, C.F. Jr. and R.E. Mesmer, 1976. The hydrolysis of cations. Wiley-Interscience.

4. Maya, L., 1982. Hydrolysis and carbonate complexation of dioxuranium (VI) in the neutral pH range at 25°C. Inorg. Chem. 21: 2895.

5. Grenthe, T., D. Ferri, F. Salvatore and G. Riccio, 1984. Studies on metal carbonate equilibria. Part 10. A solubility study of the complex formation in the uranium (VI) - carbon dioxide (g) system at 25°C. J. Chem. Soc. Dalton Trans. p. 2439.

6. Sylva, R.N. and M.R. Davidson, 1979. The hydrolyses of metal ions. Part 2. Dioxiouranium (VI). J. Chem. Soc. Dalton Trans. p. 465.

7. Analytical chemistry of Uranium. Academy Sciences of the USSR. p. 21.

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The choice of stability constant was somewhat arbitrary. The source of the constant already in THRM. DAT is unknown, thus generally these values were not used unless corroborated by the literature, or in absence of any consistent literature data. If a range of values was found, a value which represented an approximate average was selected. Eventually data acquired from Dr. Sharma will replace the fulvic acid - radium-226 binding constants used.

5.4 SELECTION OF STABILITY CONSTANTS FOR THRM DATA AND CREATION OF THE MODEL

Often literature values quoted were not from a zero ionic strength solution or were not for formation from individual components. Any corrections carried out on literature values to obtain values for input into THRM. DAT are shown.

URANIUM (IV) STABILITY CONSTANTS INCLUDED IN THRM DATA

The stability constants and uranium complexes used in THRM. DAT together with their identification numbers are presented below. U^{+4} was introduced as a new component, thus no values were in THRM. DAT. Further work could be done to collect more stability constants for U^{+4} complexes, but this is probably not necessary, since U^{+4} is likely to be present in very small quantities. The equations used and their cited references are outlined below.

Identification Number	Complex	Stability Constant in THRM DATA log K
12521	UCl^{+3}	1.35
12522	USO_4^{++}	5.47
12523	$U(SO_4)^2$	9.72
12524	U(OH)	-0.70

(1) Geochimica et Cosmoschimica Acta 42: 547 (1978). Donald Langmuir.

Redox Reaction

15050 $UO_2^{+2} \rightarrow U^{+4}$ 5.58

$UO_2^{+2} + 4H^+ + 2e \rightarrow U^{+4} + 2H_2$ 0.329 V

$$\log = \frac{-.059}{E_h}$$

$\log = 5.58$

$= \log$

Therefore $= 5.58$

(2) The Hydrolysis of Cations. C.F. Baes Jr. and R.E. Mesmer (1976) Wiley

$$K = K_o \circ \frac{A \quad B}{V_{AB}}$$

(1) $UO_2^{+2} + NO_3^- \rightarrow UO_2(NO_3)^+$ Log K = -0.62^+

u = 2, 25°C

$\log K = \log K_o + \log uo2 + \log NO_3^- - \log UO_2NO_3$

$-0.62 = \log K_o + 4(-.093) + (-.093) - (-.093)$

$-0.62 = \log K_o - 0.372$

$-0.25 = \log K_o$

* Analytical Chemistry of Uranium, Academy Sciences of the USSR. p. 21

(2) $UO_2^{+2} + H^+ + Si_2O_2(OH)_2^{2} \rightarrow UO_2SiO(OH)_3^+$

$UO_2^{+2} + H_4Si_2O_2(OH)_2^{=} + H^+$ u = 0 $K_2 = 10^{2.4*}$

$2H^+ + Si_2O_2(OH)_2 \rightarrow H_2Si_2O_2(OH)_2$ (H_4SiO_4) u = 0 $K_3 = 10^{22.7}$

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$$K_1 = \frac{[UO_2Si_1O(OH)_3^+]}{[UO_2^{+2}][H^+][Si_1O_2(OH)_2^=]} = \frac{K_2}{[UO_2Si_1O(OH)_3^+]}{[UO_2^{+2}][H2Si_1O_2(OH)_2]} \cdot \frac{K_3}{[O_2(OH)_2]}{[H^+][Si_1O_2(OH)_2]}$$

$$K = 10^{-2.4} \cdot 10^{22.2}$$

$$K_1 = 10^{20.3}$$

* Geochimica et Cosmochimica Acta 42: 547 (1978) Donald Langmuir

(3) $UO_2 + 2H^+ + 2PO_4^{-3} \rightarrow UO_2(HPO_4)_2^{-2}$ $K_1 = 6$

$UO_2 + 2PO_4^{-2} \rightarrow UO_2(HPO_4)_2^{-2}$ u = 0, 25°C $K_2 = 10^{18.3*}$

$H^+ + PO_4^{-3} \rightarrow HPO_4^{-2}$ u = 0, 25°C $K_3 = 10^{12.5}$

$$K_1 = \frac{[UO_2(HPO_4)_2^{-2}]}{[UO_2^{+2}][H]^2[PO_4]^2} = \frac{K_2}{[UO_2(HPO_4)_2^{-2}]}{[UO_2^{+2}]} \cdot \frac{K_3 - K_3}{[HPO_4^{-2}]^2}{[H^+]^2[PO_4^=]^2}$$

$K_1 = 10^{43.3}$

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5.4.1 Thorium Stability Constants Used In THRM. DAT

The stability constant data of each considered complex and their respective identification numbers are listed below.

Identification Number	Complex	Stability Constant in THRM. DAT log K
11900	ThF^{+3}	8.03
11910	ThF_2^{+2}	14.25
11920	ThF_3^{+}	18.93
11921	ThF_4	22.31
11890	$ThCl^{+3}$	1.09
11892	$ThCl_2^{+2}$	0.80
11894	$ThCl_3^{+}$	1.65
11896	$ThCl_4$	1.26
11870	$ThSO_4^{+2}$	5.45
11880	$Th(SO_4)_2$	9.73
11882	$Th(SO_4)_3^{-2}$	10.50
11884	$Th(SO_4)_4^{-4}$	8.48
12082	$Th(NO_3)^{+3}$	0.94
12084	$Th(NO_3)_2^{+2}$	0.97
11923	$Th(HPO_4)_2$	47.8
11924	$Th(HPO_4)_3^{-2}$	68.8
11925	$Th(H_2PO_4)^{+3}$	28.8
12090	$Th(OH)^{+3}$	-3.20
12091	$Th(OH)_2^{+2}$	-6.93
12092	$Th(OH)_3^{+1}$	-11.7
12093	$Th(OH)_4$	-15.9
12094	$Th_2(OH)_2$	-6.14

No literature values for complexes of thorium with carbonate or silicate were found.

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The conversion of Log K from the values presented by Langmuir, 1978 to the appropriate Log K for THRM. DAT is required. This is because complexes are not formed from individual components in the reference. We must, therefore, consider individual reactions of PO_4^{-3} and $Th^{(IV)}$

$PO_4^{-3} + H^+ \rightarrow HPO_4^{-2}$	$\log K_1 = 12.50$
$PO_4^{-3} + 2H^+ \rightarrow H_2PO_4^{-1}$	$\log K_2 = 19.9$
$PO_4^{-3} + 3H^+ \rightarrow H_3PO_4$	$\log K_3 = 21.90$
$Th^{4+} + HPO_4^{-2} \rightarrow Th(HPO_4)^{-2}$	$\log K = 10.8$
$H^+ + PO_4^{-3} \rightarrow HPO_4^{-2}$	$\log K = 12.50$
$Th^{4+} + H^+ + PO_4^{-3} \rightarrow Th(HPO_4)^{-2}$	$\log K = 23.3$
$Th^{4+} + 2HPO_4^{-2} \rightarrow Th(HPO_4)_2$	$\log K = 22.8$
$2H^+ + 2PO_4^{-3} \rightarrow 2HPO_4^{-2}$	$\log K = 12.5$
$Th^{4+} + 2H^+ + 2PO_4^{-3} \rightarrow Th(HPO_4)_2$	$\log K = 47.8$
$Th^{4+} + 3H^+ + 3PO_4^{-3} \rightarrow Th(HPO_4)_3^{-2}$	$\log K = 68.8$
$Th^{4+} + 2H^+ + PO_4^{-3} \rightarrow Th(H_2PO_4)^{+2}$	$\log K = 28.8$
$2H^+ + PO_4^{-3} \rightarrow H_2PO_4^{-1}$	$19.9 + 8.88$
$Th^{4+} + 3H^+ + PO_4^{-3} \rightarrow Th(H_3PO_4)^{+3}$	$\log K = 21.9 + 1.91 = 23.8$

5.4.2 Radium Complexes Used For THRM. DAT

Very little has been found in the literature on stability constants of Ra^{+2} complexes. However the chemistry of radium is to a large extent controlled by coprecipitation reactions with Ba and Ca sulphates. These are due to the similar size and charge of Ba^{+2} Ca^{+2} and Ra^{+2}. Accordingly, Ra speciation in our model is controlled to a large extent by Ba and its reactions.

To incorporate this co-precipitation effect into the model, the THRM data file has been modified. Barium solubility product constants were entered in place of radium constants and the ID number changed. New complex ID numbers were then used.

Unfortunately this eventuality was not forseen at the planning stage of this contract and Ba concentrations were not determined. Thus, typical concentrations values have been obtained from the literature and incorporated into the input file.

5.4.3 Ionic Strength Correction

It has been necessary to correct some of the stability constants found in the literature to a zero ionic strength value before incorporating this value into THRM. DAT.

When MINEQL carries out the calculation it uses zero ionic strength stability constants and corrects them for the ionic strength of the solution under study. It does this correction using the Davies approximation, in the subroutine IONCOR. A description of the equations involved in this subroutine follows. Thus, to correct stability constants to zero ionic strength, we have carried out the inverse calculation to IONCOR.

The log of the activity coefficient, log f, was calculated for solutions of varying ionic strength, and for Z = 1.

$\mu = 0.5$ log f = -0.157
$\mu = 1.0$ log f = -0.15
$\mu = 2.0$ log f = -0.093

Most literature values are measured at one of these ionic strengths.

and solved for log k.

$$\mu = \frac{1}{2} \sum_i [z_i^2 C_i] \qquad i: \text{ all species in solution}$$

where:

z_i = ionic charge of species i

C_i = concentration of species i

Using the fact that $Z_c = \sum_j a_j z_j$ and the expression of log f given above, we can express the corrected constant

$$\log k' = \left[\sum_j a_j a_j^2 - \left(\sum_j a_j z_j\right)^2\right] \cdot T(\mu^{1/2}) - 0.2\mu$$

$$+ \log K$$

5.4.4 Complexation With Organic Matter

The complexation of metal ions by organic matter in natural waters is thought to be an important factor in metal speciation, and likely affects the availability and toxicity of these metals to aquatic organisms. The data available in the literature is vast and always specific to given conditions such as ionic strength, temperature, pH, and source of water. Stability constants for the binding of humic and fulvic acid to trace metals have been found to vary with the above conditions. In addition, the composition of humic and fulvic acid can vary, depending upon source and method of isolation. The pK_a's for these acids also vary considerably with the above parameters. Thus, it is difficult to interpret literature values for such stability constants with the view to incorporating them into another system (i.e., Hidden Bay, Quirke Lake).

Literature values for all stability constants for fulvic acids were used for initial trial calculations. These were then amended with determined values. A table of values used is given below (Table 5.6).

Table 5.6 List of Humic and Fulvic Acid Complexes In THRM. DAT

ID NUMBER	COMPLEX	STABILITY CONSTANT
1190	Ca^{2+}-FA	3.65
1200	Ca^{2+}-HA	3.82
2665	Fe^{3+}-FA	6.00
2666	Fe^{3+}-HA	7.00
4812	Cu^{2+}-FA	7.00
4813	Cu^{2+}-HA	9.00
4911	Ba^{2+}-FA	3.50
4912	Ba^{2+}-HA	4.00
6732	Zn^{2+}-FA	4.00
6733	Zn^{2+}-HA	5.00
2086	Th^{4+}-FA	11.00
12087	Th^{4+}-HA	27.58
12471	UO_2^{2+}-FA	7.00
12473	UO_2^{2+}-HA	12.35
12527	Ra^{2+}-HA	5.53
12528	Ra^{2+}-FA	4.24
13592	H-FA	4.00

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Since the literature values are so varied, a "best guess" was used in these initial calculations. A summary of stability constants used in THRM DATA follows:

4812	$Cu^{+2} + FA^{-} \rightarrow CuFA^{+}$	log k = 5.00
6732	$Zn^{+2} + FA^{-} \rightarrow ZnFA^{+}$	log k = 4.00
2662	$Fe^{+3} + FA^{-} \rightarrow FeFA^{=}$	log k = 6.00
13592	$H^{+} + FA^{-} \rightarrow HFA$	log k = 4.00
12471	$UO_2^{+2} + FA^{-} \rightarrow UO_2FA^{+}$	log k = 6.00
12086	$Th^{++4} + FA^{-} \rightarrow ThFA^{+3}$	log k = 10.00

5.5 CREATION OF FINAL MODEL

From the data outlined in the previous sections, files were tabulated incorporating average values for four environments, Hidden Bay water and interstitial water, Quirke Lake water and interstitial water. These four files are presented in Table 5.7. Initial runs were performed with the data files and ambient pH and E_h conditions for the water phase samples. The program was then modified to conform to experimental data. The chief mechanism under investigation was organic complexation of trace metals. Our most reliable data was obtained for copper and accordingly, copper was used to evaluate our model. Model and experimental data both should show a similar percentage of organically bound copper. Once this was performed, a model was created by running the average data files at a number of pH and E_h conditions. At each of these runs, the percentage contribution of each species component was given by the model. In addition, the actual concentration of the species was also printed. The composition data was then used to construct the diagrams presented in Figures 5.1, 5.2, 5.3, 5.4 and 5.5. Each of these diagrams show the change in the percentage contribution of a given component with varying pH. It is possible to use the three-dimensional plotting routine to look at variation of a given parameter over E_h and pH conditions that it is likely to encounter. Examples of the computer print-out of our model system are appended to this report and selected examples of variations of uranium and copper speciation with changing E_h and pH of different environments are given in a separate volume. These data are representative of the types of information that is available using this form of model.

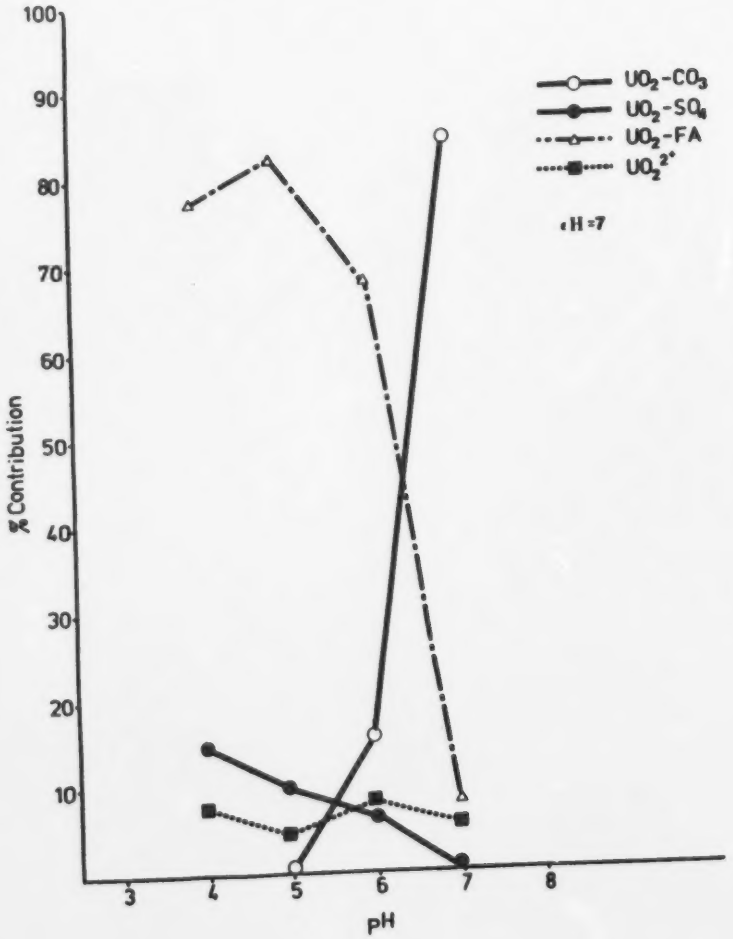

Figure 5.1

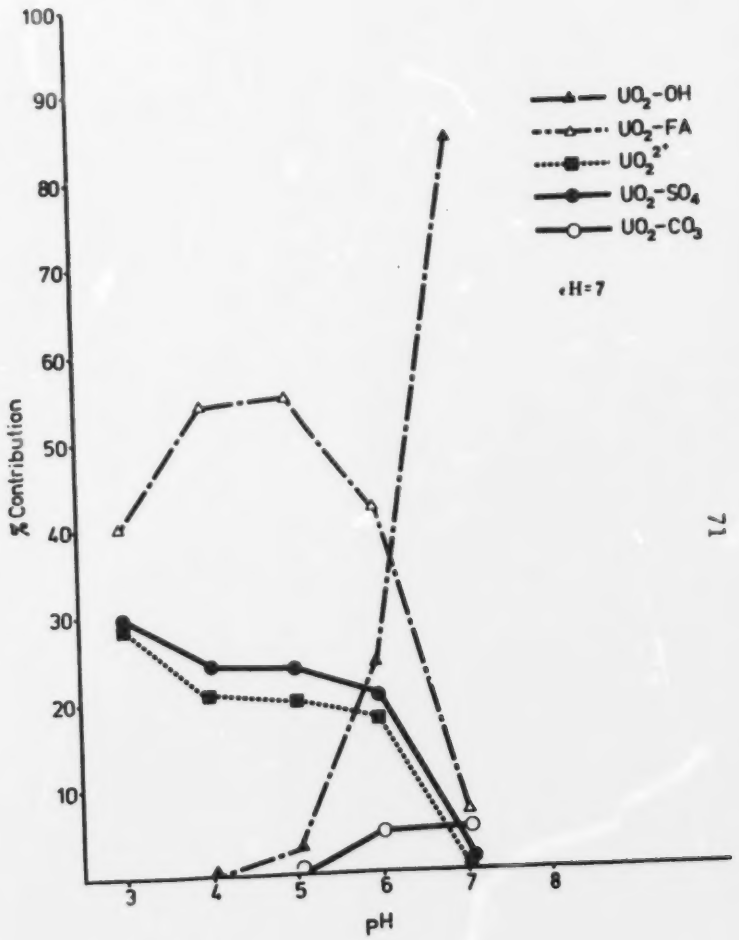

Figure 5.2

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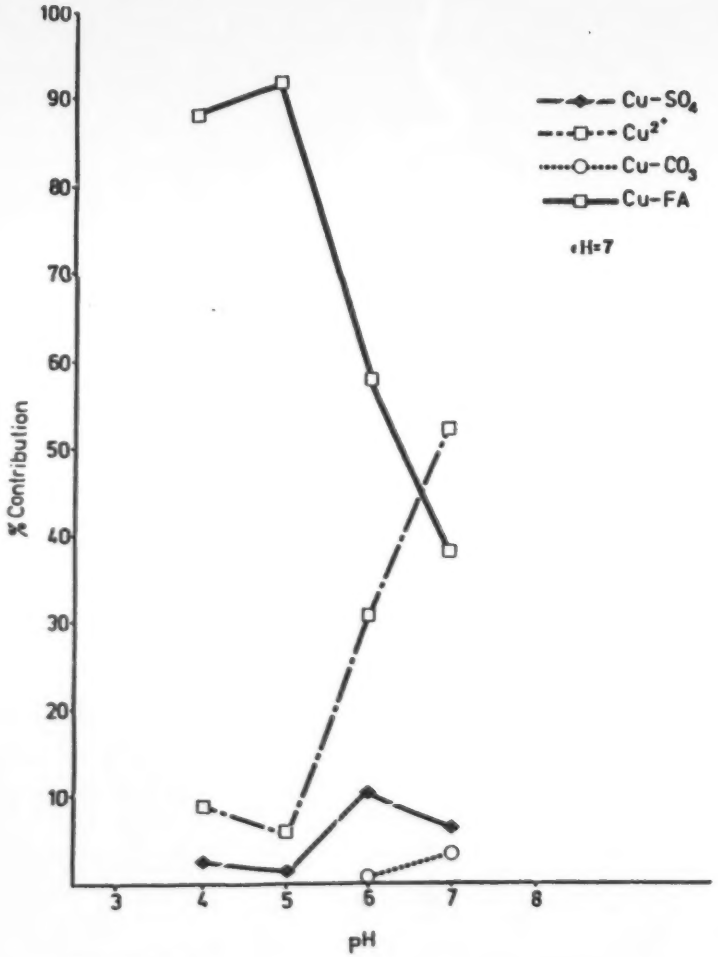

Figure 5.3

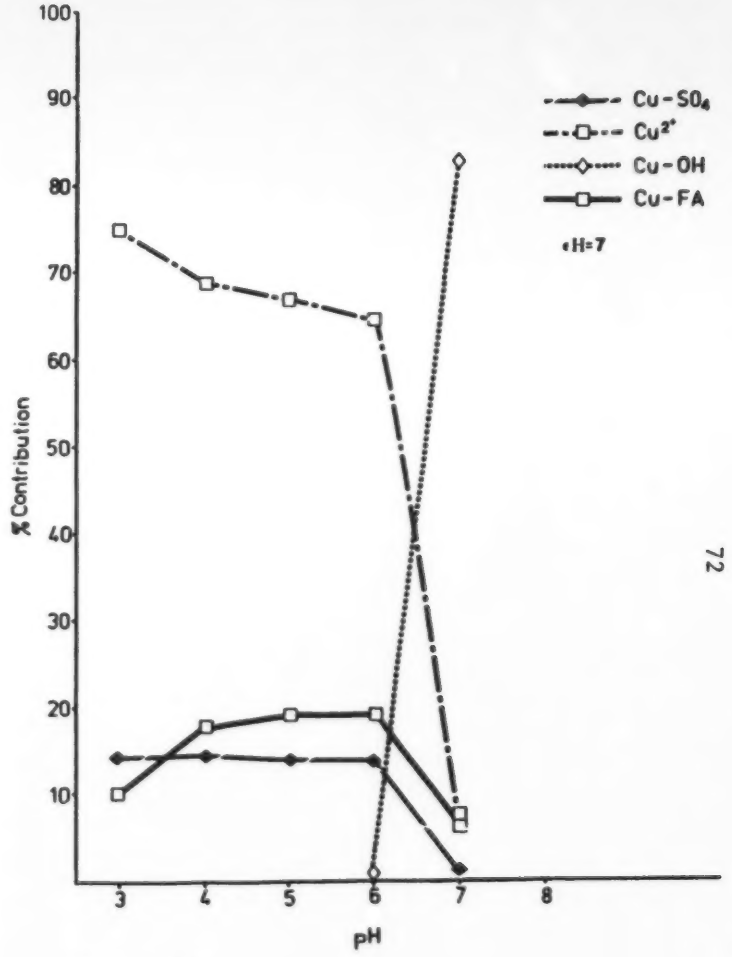

Figure 5.4

DOBROCKY SEATECH

Quirke Lake Pore Water

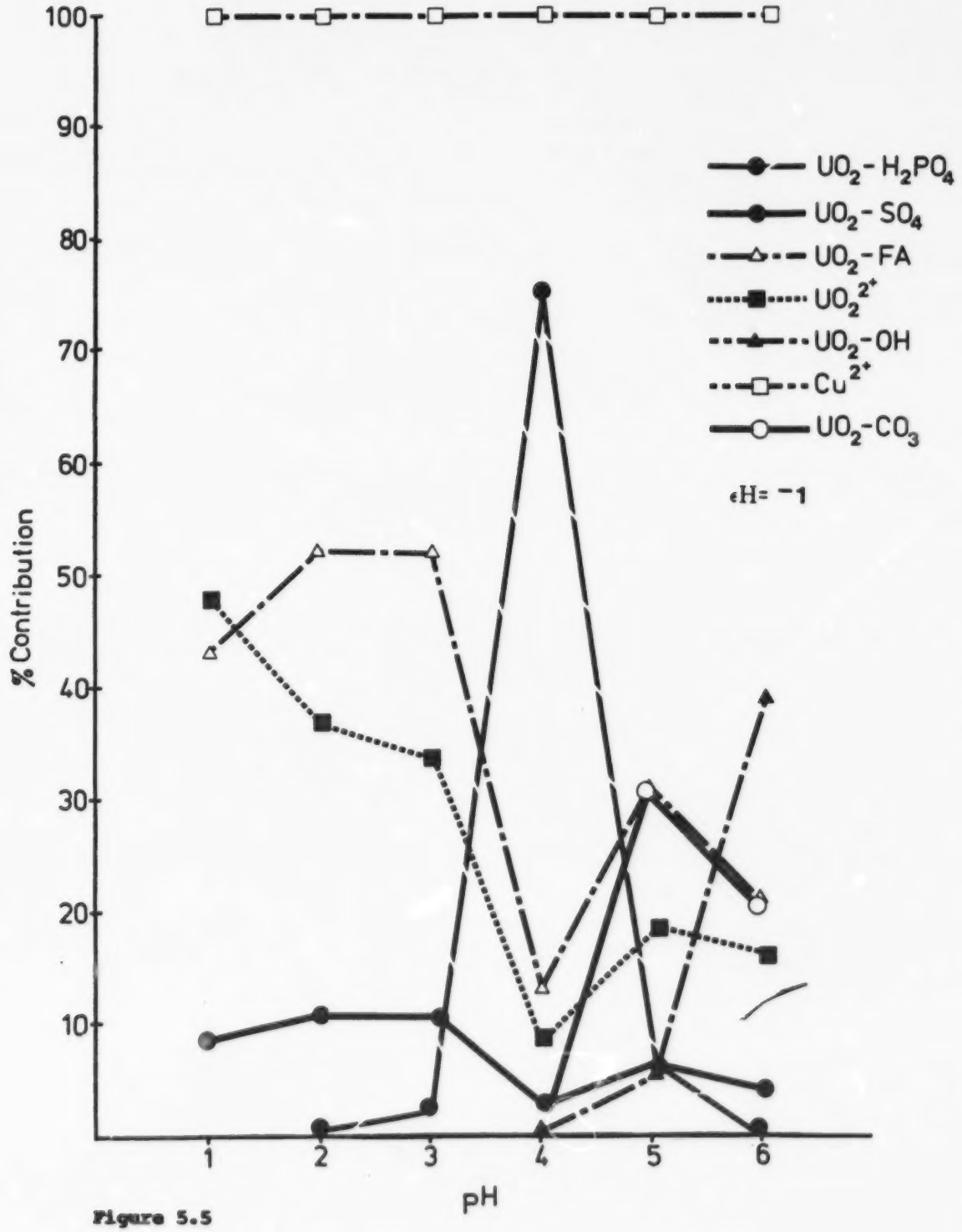

Figure 5.5

DOBROCKY SEATECH

The speciation of copper is shown in Figures 5.3 and 5.4, Hidden Bay samples average at about a pH of 6 and E_h values are probably around 7 (although the variation with E_h is much less marked then with pH). Thus, from Figure 5.3, the percent of copper associated with fulvic acid is approximately 60%. This corresponds well to experimental data. Similarly, with the Quirke Lake site, experimental data fit well to the model. In this case ambient pH is again around 6 giving a fulvic acid and copper association of around 20% of the total copper. This data also fits with experimental data. Unfortunately, organic complexation experiments with uranium in our own laboratory were unsuccessful and data from the University of Waterloo, while useful were not able to clarify the percent of organically bound uranium or thorium. Accordingly, modification of the model to experimental data of this type could not be performed. However, now the model has been created and stability constants for these elements as well as radium have been added, fine tuning can be performed on an on-going basis. Table 5.8 shows all the pH and E_h permutations that were used in our model and much of this data has been made available to the National Uraniums Tailings Program (N.U.T.P.) operating instructions for the model are also enclosed with the data set supplied to N.U.T.P.

Table 5.7 Average File Concentrations

Hidden Bay Pore Water Average

Ionic Strength = 4.05E-01*
Log F(Z=1) = .15

Concentration	Components
7.00E-05	CU_2
5.00E-02	ZN
4.00E-02	FE_3
1.00E-02	NO_3
2.00E-05	PO_4
2.00E-05	SiO_3
3.00E-02	SO_4
5.00E-05	FA
5.00E-03	CO_3^-
1.00E-06	H
0.00E+00	E^-
2.10E-09	UO_2
2.00E-14	RA
2.00E-14	TH_4
1.00E-10	BA
2.41E-08	PB

Quirke Lake Pore Water Average File

Ionic Strength = 5.16E+00
Log F(Z=1) = .17

Concentration	Components
7.00E-05	CU_2
3.50E-02	ZN
5.00E-03	FE_3
3.00E-03	NO_3
6.00E-06	PO_4
4.50E-05	SiO_3
2.00E-03	SO_4
5.00E-05	FA
5.00E-03	CO_3^-
3.36E-08	UO_2
1.00E-03	H
1.00E-02	E^-
2.00E-14	RA
2.00E-14	TH_4
1.00E-10	BA
7.22E-08	PB

Quirke Lake Average File

Ionic Strength = 4.91E-03
Log F(Z=1) = -.03

Concentration	Components
5.00E-05	NO_3
5.90E-09	PO_4
2.00E-03	SO_4
2.00E-07	SiO_3
5.00E-06	CO_3
3.50E-04	CL
4.00E-06	FA
1.50E-05	CU_2
2.00E-04	ZN
7.50E-05	FE_3
2.94E-07	UO_2
1.20E-06	H
1.00E-04	E^-
1.00E-10	BA
7.22E-08	PB
2.00E-14	RA
2.00E-14	TH_4

Hidden Bay Average File

Ionic Strength = 7.40E-03
Log F(Z=1) = -.04

Concentration	Components
4.25E-06	NO_3
3.60E-09	PO_4
3.50E-03	SO_4
3.00E-07	SiO_3
8.00E-05	CO_3
1.50E-04	CL
5.00E-06	FA
1.50E-06	CU_2
2.00E-04	ZN
2.00E-05	FE_3
2.10E-08	UO_2
1.00E-11	H
1.00E-05	E^-
1.00E-10	BA
2.00E-14	RA
9.66E-08	PB
2.00E-14	TH_4

Table 5.8 Summary of Data Output

Quirke Lake Average Five

Eh/pH	-2	-1	0	1	2	3	4	5	6	7	8	9	10
1													
2													
3				x	x	x	x	x	x	x	x	x	x
4				x	x	x	x	x	x	x	x	x	x
5				x	x	x	x	x	x	x	x	x	x
6				x	x	x	x	x	x	x	x	o	o
7				x	x	x	x	x	x	x	x	o	o

Quirke Lake Pore Water Average File

Eh/pH	-2	-1	0	1	2	3	4	5	6	7	8	9	10
1		x	x	x	x	x							
2		x	x	x	x	x							
3		x	x	*x	x	x							
4		x	x	x	x	x							
5		x	x	x	*x	x							
6		x	x	x	x	x							

Hidden Bay Pore Water Average File

Eh/pH	-2	-1	0	1	2	3	4	5	6	7	8	9	10
1		o	x	x	x	x							
2		o	x	x	x	x							
3		x	x	x	x	x							
4		x	x	x	x	x							
5		x	x	x	x	x							
6		x	x	x	x	x							
7		o	x	x	o	x							

Hidden Bay Average File

Eh/pH	-2	-1	0	1	2	3	4	5	6	7	8	9	10	11
1														
2														
3														
4					x	x	x	x	x	x	x	x	x	x
5					x	x	x	x	x	x	x	x		
6				x	x	x	x	x	x	x	x	x		
7				x	x	x	x	x	x	x	x			
8					x									

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List of Components and Identification Numbers
and Example of Computer Printout

Table 1. List of Components and Identification Numbers in THRM DATA

1	Ca^{+2}
2	Mg^{+2}
3	Sr^{+2}
4	K^{+}
5	Na^{+}
6	Fe^{+3}
7	Fe^{+2}
8	Mn^{+2}
9	Cu^{+2}
10	Ba^{+2}
11	Cd^{+2}
12	Zn^{+2}
13	Ni^{+2}
14	Hg^{+2}
15	Pb^{+2}
16	Co^{+2}
17	Co^{+3}
18	Ag^{+}
19	Cr^{+3}
20	Al^{+3}
21	Cs^{+}
22	Li^{+}
23	Be^{+2}
24	Sc^{+3}
25	TiO^{+2}
26	Sn^{+2}
27	Sn^{+4}
28	La^{+3}
29	Ce^{+3}
30	Au^{+}
31	Th^{+4}
32	UO_2^{+2}
33	Cu^{+}
34	U^{+4}
35	Ra^{+2}
50	H^{+}
99	e^{-}
101	CO_3^{-2}
102	SO_4^{-2}
103	Cl^{-}
104	F^{-}
105	Br^{-}
106	I^{-}
107	NH_3
108	S^{-2}
109	PO_4^{-3}
110	$P_2O_4^{-4}$
111	$P_3O_{10}^{-5}$
112	$SiO_2(OH)_2^{-2}$
113	$S_2O_3^{2-}$
114	CN^{-}
115	AC^{-}
148	$B(OH)_4^{-}$
149	SO_3^{-2}
150	SCN^{-}
151	NH_2OH
154	AsO_4^{-3}
155	HVO_4^{-2}
156	SeO_3^{-2}
157	NO_3^{-}
158	TRIS
159	FA

Table 2 List of Components, Identification Numbers & Stability Constants

Identification Number	Complex	Stability Constant in THRM DATA log K
12150	UO_2^+	5.10
12160	UO_2F_2	8.90
12170	$UO_2F_3^-$	11.40
12180	$UO_2F_4^=$	12.60
12140	UO_2Cl^-	0.90
12190	UO_2Br^+	0.30
12472	$UO_2NO_3^+$	-0.25
12120	$UO_2(SO_4)$	3.00
12130	$UO_2(SO_4)_2^=$	4.60
12480	$UO_2(OH)^+$	-5.8
12492	$(UO_2)_2(OH)_2$	-5.89
12494	$(UO_2)_3(OH)_5$	-16.2
12100	$UO_2(CO_3)_2$	16.8
12110	$UO_2(CO_3)_3^{-4}$	21.4
12096	$UO_2(CO_3)$	9.5
12192	$UO_2S_1O(OH)_3$	20.3
12194	$UO_2(HPO_4)_2^=$	43.3
SOLIDS		
21390	$UO_2(CO_3)$	14.4
21420	$UO_2(OH)_2$	-5.7

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Legend to Table 2

*

AC	=	acetate	NOC	=	nocardamine (desferri-ferrioxamine)
ACAC	=	acetylacetone	PHTH	=	phthalate
CIT	=	citrate	ARG	=	arginine
OX	=	oxalate	ORN	=	ornithine
SAL	=	salicylate	LYS	=	lysine
TART	=	tartrate	HIS	=	histidine
EN	=	enthylenediamine	ASP	=	aspartate
DIP	=	dipyridyl	SER	=	serine
SUSAL	=	sulfosalicylate	ALA	=	alanine
GLY	=	glycine	TYR	=	tyrosine
GLUT	=	glutamate	MET	=	methionine
PIC	=	picolinate	VAL	=	valine
NTA	=	nitrilotriacetate	THR	=	threonine
EDTA	=	ethylenediamine-tetraacetate	PHE	=	phenylalanine
DCTA	=	1,2-diaminocyclohexane tetraacetate	ISO	=	isoleucine
CYST	=	cysteine	LEU	=	leucine
PRO	=	proline	TRIS	=	tris (hydroxymethyl) - aminomethane
FA	=	fulvic acid			

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OUTPUT DATA: ITERATIONS = 28

ID	X	LOGX	T	Y	SPECIES
35	2.00E-14	-13.70	2.00E-14	-8.00E-26	RA
12	3.29E-02	-1.48	3.50E-02	-2.72E-11	ZN
31	2.41E-20	-19.62	2.00E-14	-7.40E-20	TH4
157	3.00E-03	-2.52	3.00E-03	-5.98E-19	NO3
10	1.00E-10	-10.00	1.00E-10	-1.34E-23	BA
112	7.99E-17	-16.10	4.50E-05	-8.13E-20	SIO3
102	1.47E-03	-2.83	2.00E-03	2.38E-12	SO4
159	2.65E-06	-5.58	5.00E-05	3.72E-12	FA
15	6.84E-08	-7.17	7.22E-08	7.26E-18	PB
32	7.78E-11	-10.11	3.36E-08	-2.97E-14	UO2
9	3.98E-12	-11.40	7.00E-05	0.00E+00	CU2
6	3.04E-15	-14.52	5.00E-03	-1.08E-19	FE3
50	1.00E-05	-5.00	1.00E-03	0.00E+00	H
99	1.00E+00	.00	1.00E-02	0.00E+00	E-
109	1.77E-14	-13.75	6.00E-06	0.00E+00	PO4
101	8.89E-09	-8.05	5.00E-03	0.00E+00	CO3-

ID	C	LOGC	LOGK	SPECIES:	TYPE I - COMPONENTS
9	3.98E-12	-11.40	.00	CU2	1
12	3.29E-02	-1.48	.00	ZN	1
6	3.04E-15	-14.52	.00	FE3	1
157	3.00E-03	-2.52	.00	NO3	1
109	1.77E-14	-13.75	.00	PO4	1
112	7.99E-17	-16.10	.00	SIO3	1
102	1.47E-03	-2.83	.00	SO4	1
159	2.65E-06	-5.58	.00	FA	1
101	8.89E-09	-8.05	.00	CO3-	1
32	7.78E-11	-10.11	.00	UO2	1
15	6.84E-08	-7.17	.00	PB	1
10	1.00E-10	-10.00	.00	BA	1
35	2.00E-14	-13.70	.00	RA	1
31	2.41E-20	-19.62	.00	TH4	1

ID	C	LOGC	LOGK	SPECIES:	TYPE II - COMPLEXES			
13592	6.17E-08	-7.21	3.37	FA 1	H	1		
13595	2.07E-09	-8.68	-13.68	H -1				
2070	8.96E-16	-15.05	2.30	SO4 1	FE3	1		
2080	7.73E-18	-17.11	3.07	SO4 2	FE3	1		
2170	3.82E-16	-15.42	17.85	FE3 1	H	1	PO4	1
2190	2.01E-14	-13.70	21.92	SIO3 1	FE3	1	H	1
2665	1.02E-16	-15.99	4.10	FA 1	FE3	1		
2670	1.41E-12	-11.85	-2.33	FE3 1	H	-1		
2680	6.81E-11	-10.17	-5.65	FE3 1	H	-2		
2690	2.71E-21	-20.57	-21.05	FE3 1	H	-3		
2700	2.24E-17	-16.65	-22.13	FE3 1	H	-4		
2710	4.63E-22	-21.33	-2.30	FE3 2	H	-2		
3920	9.61E-15	-14.02	5.43	CU2 1	CO3-	1		
3930	1.35E-19	-18.87	8.63	CU2 1	CO3-	2		
3932	3.83E-14	-13.42	11.03	CU2 1	H	1	CO3-	1
3940	6.35E-14	-13.20	1.03	SO4 1	CU2	1		
4010	1.71E-16	-15.77	14.38	CU2 1	H	1	PO4	1
4012	5.72E-13	-12.24	4.73	FA 1	CU2	1		
4840	2.42E-15	-14.62	-8.22	CU2 1	H	-1		
4842	3.83E-16	-15.42	-14.02	CU2 1	H	-2		
4844	6.31E-24	-23.20	-26.80	CU2 1	H	-3		
4846	2.15E-31	-30.67	-39.27	CU2 1	H	-4		
4850	3.83E-24	-23.42	-10.62	CU2 2	H	-2		
4911	4.54E-14	-13.34	2.23	BA 1	FA	1		
5060	7.64E-19	-18.12	-13.12	BA 1	H	-1		
5954	3.16E-06	-5.50	4.03	ZN 1	CO3-	1		
5956	3.16E-04	-3.50	11.03	ZN 1	H	1	CO3-	1
5960	5.25E-04	-3.28	1.03	ZN 1	SO4	1		
6060	1.78E-07	-6.75	13.48	ZN 1	H	1	PO4	1
6732	4.73E-05	-4.33	2.73	ZN 1	FA	1		
6740	5.02E-07	-6.30	-9.82	ZN 1	H	-1		
6745	1.26E-07	-6.90	-15.42	ZN 1	H	-2		
6750	1.65E-14	-13.78	-27.30	ZN 1	H	-3		
6760	7.09E-22	-21.15	-39.67	ZN 1	H	-4		
8060	8.27E-10	-9.08	6.13	PB 1	CO3-	1		
8070	1.85E-14	-13.73	9.53	PB 1	CO3-	2		
8080	2.74E-09	-8.56	1.43	SO4 1	PB	1		
8520	2.62E-10	-9.58	-7.42	PB 1	H	-1		
8530	1.04E-14	-13.98	-16.82	PB 1	H	-2		
8540	2.72E-20	-19.57	-27.40	PB 1	H	-3		

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8550	4.86E-16	-15.31	-5.98	PB	2	H	-1			
11870	2.94E-20	-19.53	2.92	TH4	1	SO4	1			
11880	4.48E-20	-19.35	5.93	TH4	1	SO4	2			
11882	3.89E-22	-21.41	6.70	TH4	1	SO4	3			
11884	1.01E-25	-25.00	5.95	TH4	1	SO4	4			
11923	9.57E-16	-15.02	42.10	TH4	1	H	2	PO4	2	
11924	1.90E-14	-13.72	62.15	TH4	1	H	3	PO4	3	
11925	3.81E-18	-17.42	25.95	TH4	1	H	2	PO4	1	
12082	3.41E-23	-22.47	-.33	TH4	1	NO3	1			
12084	1.23E-25	-24.91	-.25	TH4	1	NO3	2			
12086	1.88E-17	-16.73	8.47	TH4	1	FA	1			
12090	1.71E-19	-18.77	-4.15	TH4	1	H	-1			
12091	7.41E-19	-18.13	-8.51	TH4	1	H	-2			
12092	6.07E-19	-18.22	-13.60	TH4	1	H	-3			
12093	3.83E-18	-17.42	-17.80	TH4	1	H	-4			
12094	3.75E-35	-34.43	-5.19	TH4	2	H	-2			
12096	1.19E-10	-9.93	8.23	U02	1	C03-	1			
12100	2.10E-11	-10.68	15.53	U02	1	C03-	2			
12110	1.37E-13	-12.86	21.40	U02	1	C03-	3			
12120	6.22E-12	-11.21	1.73	SO4	1	U02	1			
12130	3.65E-13	-12.44	3.33	SO4	2	U02	1			
12192	6.73E-13	-12.17	19.03	SI03	1	U02	1	H	1	
12194	3.33E-08	-7.48	40.13	U02	1	H	2	PO4	2	
12471	1.12E-10	-9.95	5.73	FA	1	U02	1			
12472	3.06E-14	-13.51	-.88	NO3	1	U02	1			
12480	5.95E-12	-11.23	-6.12	U02	1	H	-1			
12492	3.68E-17	-16.43	-6.22	U02	2	H	-2			
12494	3.34E-23	-22.48	-17.15	U02	3	H	-5			
12528	4.98E-17	-16.30	2.97	RA	1	FA	1			
12529	1.53E-22	-21.82	-13.12	RA	1	H	-1			
12530	3.28E-04	-3.48	9.57	H	1	C03-	1			
12540	3.16E-03	-2.50	15.55	H	2	C03-	1			
12550	5.44E-07	-6.26	1.57	SO4	1	H	1			
12600	6.29E-08	-7.20	11.55	H	1	PO4	1			
12610	3.68E-06	-5.43	18.32	H	2	PO4	1			
12620	1.77E-09	-8.75	20.00	H	3	PO4	1			
12710	2.34E-09	-8.63	12.47	SI03	1	H	1			
12720	4.50E-05	-4.35	21.75	SI03	1	H	2			

ID	C	LOGC	LOGK	SPECIES:	TYPE III - FIXED SOLIDS
99	8.19E-03	-2.09	.00	E-	1
50	7.28E-03	-2.14	5.00	H	1

ID	C	LOGC	LOGK	SPECIES:	TYPE IV - PRECIPITATED SOLIDS				
21460	1.67E-03	-2.78	3.55	FE3	3	H	-8	E-	1
21510	7.00E-05	-4.15	11.40	CU2	1	E-	2		
20650	1.01E-06	-6.00	31.95	ZN	3	PO4	2		
20630	1.20E-03	-2.92	9.53	ZN	1	C03-	1		

ID	C	LOGC	LOGK	SPECIES:	TYPE V - DISSOLVED SOLIDS				
20460	1.77E-29	-28.75	32.95	CU2	3	PO4	2		
20500	1.92E-10	-9.72	-8.32	CU2	1	H	-2		
20510	4.81E-10	-9.32	8.73	BA	1	C03-	1		
20520	1.27E-03	-2.90	9.93	BA	1	SO4	1		
20440	3.68E-17	-16.43	4.42	CU2	2	H	-2	C03-	1
20430	8.18E-12	-11.09	8.36	CU2	1	C03-	1		
20660	4.51E-01	-.35	17.23	ZN	1	SI03	1		
20700	1.59E-03	-2.80	-11.32	ZN	1	H	-2		
20780	1.04E-03	-2.98	12.23	PB	1	C03-	1		
20790	8.98E-12	-11.05	16.55	PB	3	H	-2	C03-	2
20800	2.74E-04	-3.56	6.43	SO4	1	PB	1		
20830	2.93E-16	-15.53	10.38	PB	1	H	1	PO4	1
20840	1.79E-11	-10.75	38.25	PB	3	PO4	2		
20850	3.45E-19	-18.46	53.62	PB	5	H	-1	PO4	3
20860	3.09E-19	-18.51	1.92	SI03	1	PB	2	H	-2
20910	1.65E-05	-4.78	-7.62	PB	1	H	-2		
21380	7.64E-49	-48.12	-48.50	TH4	1	H	-4		
21390	9.42E-06	-5.03	13.13	U02	1	C03-	1		
21420	7.49E-07	-6.13	-6.02	U02	1	H	-2		
21430	9.61E-14	-13.02	8.73	RA	1	C03-	1		
21431	2.53E-07	-6.60	9.93	RA	1	SO4	1		
21440	2.26E-02	-1.65	24.45	SI03	1	H	2		
20280	4.81E-06	-5.32	22.95	FE3	1	PO4	1		
21500	1.85E-36	-35.73	-48.57	PB	1	H	-4	E-	-2

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20310	3.41E-04	-3.47	-3.95	FE3	1	H	-3	

ID	C	LOGC	LOGK	SPECIES:	TYPE VI - SPECIES NOT CONSIDERED		
25000	9.98E-02	-1.00	17.05	H	2	CO3-	1

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QUIRKE LAKE PORE WATER AVERAGE FILE

PERCENTAGE DISTRIBUTION OF COMPONENTS

RA	99.8	PERCENT BOUND IN SPECIES # 35	RA	1					
ZN	94.0	PERCENT BOUND IN SPECIES # 12	ZN	1					
	1.5	PERCENT BOUND IN SPECIES # 5960	ZN	1	SO4	1			
	3.4	PERCENT BOUND IN SPECIES #20630	ZN	1	CO3-	1			
TH4	4.8	PERCENT BOUND IN SPECIES #11923	TH4	1	H	2	PO4	2	
	95.1	PERCENT BOUND IN SPECIES #11924	TH4	1	H	3	PO4	3	
NO3	100.0	PERCENT BOUND IN SPECIES # 157	NO3	1					
BA	100.0	PERCENT BOUND IN SPECIES # 10	BA	1					
SIO3	100.0	PERCENT BOUND IN SPECIES #12720	SIO3	1	H	2			
SO4	73.7	PERCENT BOUND IN SPECIES # 102	SO4	1					
	26.2	PERCENT BOUND IN SPECIES # 5960	ZN	1	SO4	1			
FA	5.3	PERCENT BOUND IN SPECIES # 159	FA	1					
	94.6	PERCENT BOUND IN SPECIES # 6732	ZN	1	FA	1			
PB	94.7	PERCENT BOUND IN SPECIES # 15	PB	1					
	1.1	PERCENT BOUND IN SPECIES # 8060	PB	1	CO3-	1			
	3.8	PERCENT BOUND IN SPECIES # 8080	SO4	1	PB	1			
UO2	99.0	PERCENT BOUND IN SPECIES #12194	UO2	1	H	2	PO4	2	
CU2	100.0	PERCENT BOUND IN SPECIES #21510	CU2	1	E-	2			
FE3	100.0	PERCENT BOUND IN SPECIES #21460	FE3	3	H	-8	E-	1	
H	212.4	PERCENT BOUND IN SPECIES #21460	FE3	3	H	-8	E-	1	
E-	92.3	PERCENT BOUND IN SPECIES #21460	FE3	3	H	-8	E-	1	
	7.7	PERCENT BOUND IN SPECIES #21510	CU2	1	E-	2			
PO4	3.0	PERCENT BOUND IN SPECIES # 6060	ZN	1	H	1	PO4	1	
	1.1	PERCENT BOUND IN SPECIES #12194	UO2	1	H	2	PO4	2	
	1.0	PERCENT BOUND IN SPECIES #12600	H	1	PO4	1			
	61.3	PERCENT BOUND IN SPECIES #12610	H	2	PO4	1			
	33.6	PERCENT BOUND IN SPECIES #20650	ZN	3	PO4	2			
CO3-	6.3	PERCENT BOUND IN SPECIES # 5956	ZN	1	H	1	CO3-	1	
	6.6	PERCENT BOUND IN SPECIES #12530	H	1	CO3-	1			

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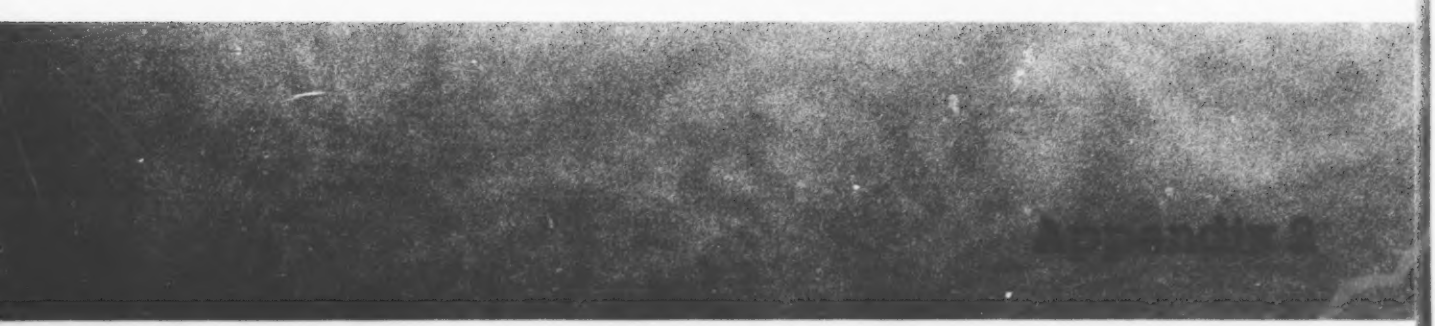
63.1	PERCENT BOUND IN SPECIES #12540	H	2	CO3-	1
23.9	PERCENT BOUND IN SPECIES #20630	ZN	1	CO3-	1

Miscellaneous Information



ORGANIZATION OF INPUT

1) TITLE

2) IONIC STRENGTH (FG_2)(XM_u)

Description of Data	Format
one group for components	
IDXT, GXT, IT	(I5,2X,F7.2,E7.2)
.	
.	
.	
blank card	
one group for each type of species	
LTYPE	(I5)
IDYT,*GKT,*(IDX(J),IAT(J),J=1,4)	(I5,2X,F7.2,4(I4,I3))
.	
.	
.	
blank card	
one card to terminate all input	
blank card	

+ See following page for description. Sample input data is given in Table 5.

* Optional input. See text.

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+ Description of Symbols

For each component a card where:

IDXT = component identification number

GXT = guess for the $\log_{10}$ of the concentration (molar) of the free component

TT = analytical (total) concentration (molar) of the component

For each species <u>type</u> to which species are to be assigned a card where:

LTYPE = type of species

followed by a card for each species to be assigned to that type where:

IDYT = species identification

*GKT = $\log_{10}$ of formation constant for the species

*(IDXT(J), IAT(J), J = 1,4) = stoichiometry of the species:

IDXT = component identification number, and IAT = stoichiometric coefficient of that component.

* Optional Input. See text.

INTERPRETATION OF FORMATION CONSTANTS

MINEQL considers the formation of species from the individual components; therefore, overall formation constants are considered and not stepwise formation constants. It is these overall formation constants that are stored in the THRM. DAT file. However, in the case of hydroxides, the species are considered to be formed by the hydrolysis of the cation.

i.e. $M^{++} + H_2O \quad M(OH)^+ + H^+$

$$K_1^* = \frac{[M(OH)^+]\ [H^+]}{[M^{++}]}$$

K_1^* is the constant required by MINEQL. However, often the formation constants for hydroxides are those for reaction of the cation with OH^-.

$$M^{++} + OH^- \quad M(OH)^+$$

$$K_1 = \frac{[M(OH)^+]}{[M^{++}][OH^-]}$$

These K_1 values can be converted to K_1^* values by multiplying by Kw.

$$Kw = 10^{14.0} = [H^+][OH^+]$$

$$(K_1)(Kw) = \frac{[M(OH)+]\ [H^+]}{[M^{++}]} = K_1^*$$

Generally, for complexes with n hydroxide groups

$$(Kn)(Kw)^n = K_n^*$$

use in MINEQL

In the case of solids, the formation constant is taken to be the inverse of the Ksp.

i.e. $AgCl \quad Ag^+ Cl^- \quad K_{sp}\ [Ag^+][Cl^-]$

MINEQL considers the formation of species from their components

$$Ag^+ + Cl^- \quad AgCl \quad K = \frac{1}{[Ag^+][Cl^-]} = \frac{1}{K_{sp}}$$

In the case of solid hydroxides

$$K_n^* = \frac{Kw^n}{K_{sp}}$$

These conversions between formation constants should be recalled when interpreting constants quoted in the literature with the view of including them in MINEQL calculations.

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CALCULATION OF F FACTOR

Using Na_2CO_3 standardization solution:

Example:

pH 4.2, vol. of acid = 1.800
pH 4.5, vol. of acid = 1.750
Starting vol. of acid = 0.000

Vol. of acid needed for titration = $X_1 - (X_2 - X_1)$
X_1 = mL of acid needed to titrate to 4.5
X_2 = mL of acid needed to titrate to 4.2

Thus, number of mL of acid used = 1.750 - (1.800 - 1.750)
= 1.700 mL

Therefore, 1.700 mL of 0.01N HCl is equivalent to 1 mg Na_2CO_3
For alkalinity in terms of $CaCO_3$:
1060 mg/L Na_2CO_3 is equivalent to 1000 mg/L $CaCO_3$.
Therefore, 1.700 mL of 0.01N HCl is equivalent to (1/1.06) mg $CaCO_3$.

1 mL of 0.01N HCl is equivalent to 0.5549 mg $CaCO_3$
F factors are:
For 1 mL sample aliquot:
1000/1 mL x 0.5549 = 554.9
F = 554.9 mg/mL . litre $CaCo_3$

NB: Alkalinity was very low in Hidden Bay and Quirke Lake samples, so volumes are small and $(X_2 - X_1)$ becomes very small. Also X_1 X_2.

For 0.50 mL sample aliquot:
1000/0.50 mL x 0.5549 = 1109.8
F = 1109.8 mg/mL . litre $CaCo_3$

DOBROCKY SEATECH

STORAGE REQUIREMENTS FOR MINEQL PROGRAM

The approximate storage requirements for MINEQL are given below. The data are based on 8 bit bytes, 4 byte words, 1 word variables for FORTRAN IV G-1 on an IBM 370/168. To change the dimensions of the arrays only two major changes are necessary.

1) Change NXDIM and NYDIM in MAIN
2) Change all of the dimensions in all of the COMMON/VAR/statements. This can be done conveniently with a TSO editor.

Passive Storage

1)	Thermodynamic Data Deck	1500 cards	120K
2)	Source Program Deck	600 cards	48K

Active Storage

1)	Objective Program minus Storage for arrays	18K
2)	Storage for Arrays	
	a) 10 components, 100 species	7K
	b) 25 components, 300 species	38K
	c) 30 components, 2000 species	59K
	d) 35 components, 5000 species	84K
3)	Auxiliary Subprograms Called by linkage editor	24K
4)	I/O Buffers	24K

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Total Core for Execution:

Components	Species	Core
10	100	73K
25	300	104K
30	400	125K
35	500	150K

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